

# History of Large Area Coatings

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## Why Coat Glass?

Glass was first used as a glaze for stone beads in Mesopotamia at around 12,000 BCE [1]. It could thus be argued that glass was the first material formulated by man. Since the invention of glass, its value has been increased by adding color. Many examples exist from early Phoenicia to Venice to the “stained” glass found in churches in Europe. Today, greater options exist for modifying glass aesthetics and appearance, as well as controlling heating, cooling, and the internal daylight balance. Glass performance can now be modified through coatings applied to the surface of the glass, rather than coloring agents added to the bulk melt. A prerequisite for coating glass is that the surface must be very flat because the coating will accentuate any striations. Sheet glass making processes such as rolling and drawing do not provide the necessary flatness. Pilkington’s [2] 1950s invention of the “float” process produces extremely flat glass in large quantity; float glass allowed the rapid growth of coated glass in the late 1970s and 1980s. Moreover, the float process makes glass available in large sizes, which are cut from the flat glass ribbon. Large area coating equipment has been designed to accommodate approximately 100 in x 144 in (U.S. standard) and 3.21 m x 6.00 m (European jumbo) glass substrates.

## History of Glass Coating

Many large area processes have been used to coat glass over the years. One of the first architectural coated glass products was introduced by Pittsburgh Plate Glass (now PPG Industries, Inc.) in the 1960s, using a pyrolytic or hot chemical process [3]. This was known as “light heat reflecting” (or LHR) glass. At about the same time Saint-Gobain used a simple batch resistance evaporation method [4] to deposit gold (which was only \$30 an ounce at the time). PPG then developed a wet process called Solarban that had a marked improvement in performance over the LHR glass. Libbey-Owens-Ford (LOF, now Pilkington), was the first to use an in-line vacuum process, rather than a batch process [5]. Figure 1 shows the LOF coater, built by Airco Temescal and made operational in Toledo, OH, in 1968, which was based on electron beam evaporation onto vertical 120 in x 144 in glass (two lites per load). The coating was called Vari-Tran (variable light transmission) and consisted of evaporated metals such as chromium or aluminum with a silica overcoat.

Also in the 1960s, Optical Coating Laboratory (OCLI, now JDS UniPhase) in Santa Rosa, CA, built and operated the multilayer automatic coater (MAC) to coat 32 inch x 50 inch glass substrates with up to six-layer coatings using sequentially connected electron beam evaporation chambers. The substrates moved through the coating chambers on a system of carriers in sub 60-second cycle times. While 32-in. x 50-in. is not large area by today’s standards, the layer stack complexity, tolerances, and machine automation set the standards for the coming larger area systems. It was 20 years before large area sputtering systems could match the coating uniformity and tolerances of the MAC.

In 1970 Leybold (now Applied Materials) built the first large area coater in Europe for BSN in France. This coater was a vertical batch coater using diode sputtering. In 1971 the invention of the planar magnetron [7] allowed sputtering at film deposition rates much higher than previously possible. At that time, Al Grubb was a young physicist working as the Technical and Production Manager of the previously

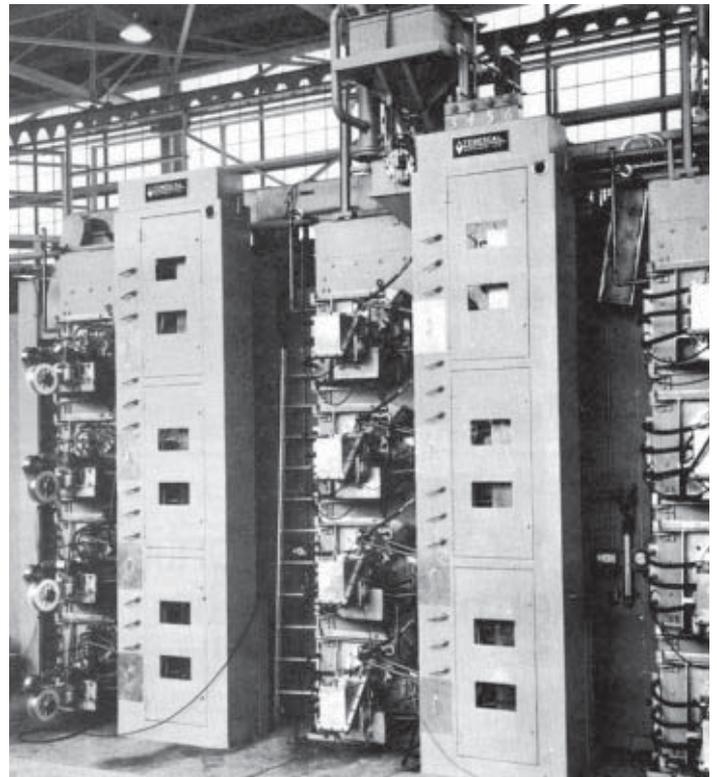


Figure 1. First large area vertical glass coating system using electron beam evaporation (1968) [6].

mentioned LOF coater. After moving to RCA in 1973, he bought one of the first R&D planar magnetron sputtering sources from Airco Temescal [8] (now Applied Materials). He put two innovations together – first, for high-volume coating production, glass should not be held vertically, but horizontally on rollers, as done in float glass manufacturing. Second, although it is not possible to evaporate down, it is easy to sputter in any direction. (Note: the electron beam coater operated by LOF needed specially developed sources pioneered by Temescal to evaporate sideways [9], and OCLI’s MAC coated from beneath onto a carrier system for the substrates.) With this vision, Al went to work for Airco Temescal in 1974, and the simple and workable in-line sputtering glass coater was invented [8].

In 1975 the first sputtered glass product, for automotive sunroofs, went into mass production. This system was made by Airco Temescal. The first sputter-coated architectural glass was made in 1977 [10] at the Guardian-Airco joint venture coating plant established in Carleton, MI. This coater, built and managed by Airco, had a load size of 78in. x 156in. with two coat zones having three planar magnetron cathodes in each zone. Airco received orders next for coaters for Pilkington in Sweden and SIV in Italy, and the large area business began growing. Today, large area coating is a worldwide commercial process. As of 2006, there are over two hundred large area sputter production coaters in place in 22 countries worldwide.

Table 1 provides key events in the recent history of large area glass coating technology. Improvements in coating technology have occurred rapidly, and applications have extended from the original sputtered

sunroofs to coated architectural and residential flat glass and curved automotive windshields.

Large-scale U.S. production of silver-based low-emissivity coatings [11] began in 1983, extending the application of coated products to the residential glazing market. The first coatings on curved substrates were introduced in 1983. A silver-based windshield coating was developed to provide an electrically conducting, optically transparent coating. This is useful for people who live in cold regions and need to eliminate ice and snow from their windshields. Subsequently, large-aperture coaters able

to accommodate deeply bent architectural glass were introduced [11].

In 1989, a significant advance was made with the development of the cylindrical rotatable magnetron cathode [12]. Rather than using a flat planar target, it uses target material made in the form of a rotating tube with the magnetron magnets and cooling water inside the tube. The continuously rotating surface offers the advantage of more target material, therefore longer production runs – critical to large area production economics. The key advantage, however, is the improved performance during reactive sputtering of dielectrics (oxide and nitride compounds).

<b>1960's</b>	<ul style="list-style-type: none"> <li>• PPG - Produced pyrolytic coatings in a batch process known as light heat reflecting, (LHR) with good durability, medium performance.</li> <li>• PPG - Wet process known as "Solarban," high performance.</li> <li>• LOF - Vacuum process on Airco Temescal electron beam evaporator (first in-line vacuum coater). 3 x 3.6 meter glass. "Varitran," high performance, good durability.</li> <li>• OCLI – MAC coater 32 in x 50 in, six layer, AR quality coatings</li> </ul>
<b>1970's</b>	<ul style="list-style-type: none"> <li>• Leybold builds vertical batch diode sputter coater for BSN.</li> <li>• Planar magnetron invented.</li> <li>• First sputtered glass product - sun roofs for cars.</li> <li>• First U.S. off-line architectural glass coater – Guardian-Airco joint venture.</li> <li>• Sputtering displaces most other large area glass coating technologies.</li> </ul>
<b>1980's</b>	<ul style="list-style-type: none"> <li>• First dedicated Ag-based low-emissivity coater.</li> <li>• Windshield coater introduced.</li> <li>• Large aperture bent glass coaters introduced.</li> <li>• Rotatable cylindrical magnetron introduced (C-MAG<sup>®</sup>).</li> </ul>
<b>1990's</b>	<ul style="list-style-type: none"> <li>• Large-scale production of silica-based optical coatings.</li> <li>• Sputter-up coating system introduced for defect-free antireflective optical films.</li> <li>• Modular coater introduced.</li> <li>• AC/DC rotary cathode introduced.</li> </ul>

Table 1. History of Coated Architectural Glass

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## History of Large Area Coatings

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Reactive sputtering with planar magnetrons resulted in a build up of thick dielectric layers in non-sputtered target areas. Such areas were prone to dielectric break-down or arcing. The cylindrical magnetron surface is continuously sputter-cleaned, significantly reducing this problem.

Previously difficult to sputter materials, such as silicon dioxide ( $\text{SiO}_2$ ) or silicon nitride ( $\text{Si}_3\text{N}_4$ ), could now be exploited.  $\text{SiO}_2$  provides a low refractive index material, which is required for many optical coatings, such as antireflection stacks.  $\text{Si}_3\text{N}_4$  provides a transparent dielectric film of extremely high chemical and mechanical durability, commonly used as a protective coating. In 1990, the first silicon-based optical films were introduced using large area sputtering with rotatable C-MAG<sup>®</sup> (cylindrical magnetron) cathodes. In 1992, this was extended to a sputter-up configuration for applying antireflection coatings on CRT (cathode ray tube) faceplates and tubes that require extremely low defect densities. Throughout the 1990s and early 2000s, improvements were made in magnetron performances (involving magnetic structures and designs); flow controllers and trim gas feed; end block designs for holding the rotating targets; target materials and constructions; power supplies for total power, arc control, and AC or pulsed DC; in-situ and ex-situ performance monitoring; automatic coating controls; and general design and pumping of chambers and in transport of the substrate so that film uniformities of  $\pm 1\%$  can now be reached over production runs weeks long. These innovations (many discussed in more detail below) allow the economic production of complex coating designs such as antireflection coatings and double and triple silver low-emissivity coatings.

## Maturation of the Large Area Coatings Industry

By the mid 1990s, the basic shape of large area coating technology was fairly mature. The primary deposition technologies of planar or rotatable magnetrons and high power electron beam guns were in wide use. The major applications (e.g., solar control and low-emissivity coatings on glass) were in widespread production. The next period was one of refinement, focused on improved product performance, efficiency, and cost reduction. These advances focused on the magnetron sources and new ways to operate or control them, development of new target materials, and greater understanding of the effect of the substrate. In combination, these improvements allowed manufacturers to continually enhance the performance of sputtered coatings while reducing their unit production costs.

New products (e.g., switchable coatings, photovoltaics) continued to stay on the horizons of breaking into the same scale of large area mass production, without yet reaching their full potential.

## Magnetron Sources

The history of large area coating can be read as a history of the development of large area deposition sources, primarily sputtering and secondarily electron beam. From the 1970s to the 1980s saw the introduction and maturation of the planar magnetron source. The cylindrical rotatable magnetron was introduced at the end of the 1980s and refined in the 1990s. Up through the early 1990s, all these magnetrons utilized DC sputtering for both metallic and reactive depositions.

With the introduction of mid-frequency/AC sputtering on dual sources in the mid 1990s, a new generation of source development occurred. In mid-frequency sputtering, each element of a dual source magnetron (whether planar or cylindrical) alternates as cathode or anode at a frequency generally between 20–80 kHz. Arcing due to the buildup of thin dielectric layers is eliminated, as these layers become conductive at these frequencies.

The 1997 Society of Vacuum Coaters (SVC) Technical Conference (TechCon) saw the presentation of results for mid-frequency reactive sputtering of  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ , and  $\text{TiO}_2$  on dualplanar and cylindrical magnetrons. The greater stability of the mid-frequency process allowed for sputtering either closer to the knee of the hysteresis curve by the addition of argon or in the transition zone between metallic and fully reactive sputtering with the stabilization of the process via control loops (see below). Mid-frequency sputtering with dual planar magnetrons was still limited by the static erosion groove, which limited target utilization and provided large unsputtered areas for redeposition of thick dielectric layers. Heister, Krempel-Hesse, Szczyrbowski, and Brauer [13] introduced a modified dual planar in 1998 to attempt to address these issues.

The combination of higher target utilization and complete sputtering of the target surface provided a definite advantage for the cylindrical rotatable magnetron versus the dual planar version. The elimination of the unsputtered surfaces removed the buildup of thick dielectric deposits that were sources of debris and arcing. Over time, ongoing development focused on the optimization of the dual rotating sources.

Optimization of the dual rotating sources focused on uniformity and utilization. Flexible adjustments to magnet systems were developed to modify the sputtering rate by adjusting magnetic field strength along the racetrack. This allowed fine tuning of deposition uniformity and mitigated the loss of target utilization from “end-grooving” caused by the higher erosion in the turnaround of the racetrack [14, 15].

Excessive wear in or adjacent to the turnaround region (the “cross-corner” effect) on both planar and rotatable magnetrons remained the major impediment to improved target utilization and deposition source efficiency. Progress in understanding this problem has been made through the efforts of several groups to develop advanced computer simulations of the magnetron fields and their effect on electron drift. Analysis has shown the effect of both magnetic field strength and field gradients on the electron paths through the magnetron. Changes in field strength and orientation moving through the turnaround can allow electrons to escape the racetrack, forming localized regions of higher plasma density and greater erosion [16, 17].

The optimization of the mid-frequency sputtering process required another round of redesign by equipment suppliers. The combination of mid-frequency power to the rotating seals of the dual magnetron posed exceptional challenges. At mid frequencies, currents are carried on the surface of conductors (“skin effect”), increasing the heating of sealing surfaces. Inductive heating also needs to be managed. Simultaneously, a new generation of power supply sources was developed. Within a short period of time, maximum output of mid-frequency power supplies rose from 120 kW/300 amps to 180 kW/400 amps. Equipment capabilities grew quickly in this environment [18, 19]. The main features of a typical high power mid-frequency power supply for large area coating are shown in Figure 2 [20].

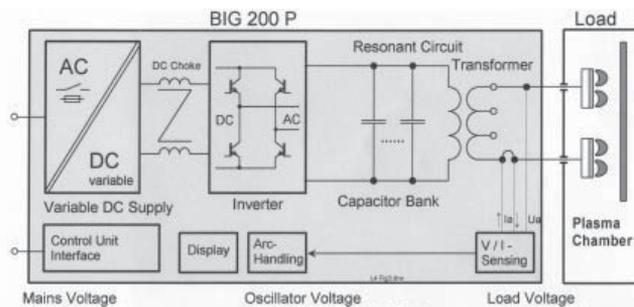


Figure 2. Block diagram of a typical mid-frequency power supply showing the oscillator circuit based on high-power insulating gate bipolar transistor (IGBT) devices and the matching network [20].

Several other power supply technologies were explored in search of new capabilities and features for film deposition. Extensive work continues on pulsed DC as an alternative to mid-frequency sputtering. Unipolar and bipolar pulsed DC offers the ability to control the ion bombardment of the substrate. By controlling the combination of unipolar and bipolar pulses and associated ion bombardment, features such as the surface roughness or stress of deposited films such as SiO<sub>2</sub> can be controlled. With proper adjustment, DC pulse sputtering can control arcing but requires "hiding" the anode or otherwise protecting the anode surfaces from coating and "disappearing" [21-23].

The extreme limit of pulse sputtering is seen in the study of high-power low-frequency pulses. "HPPMS" or high-power pulse magnetron sputtering, uses 0.5–1.0 MW pulses at 100 HZ frequency for reactive sputtering with pulse widths of 100–150 microseconds. Initial results for reactive sputtering of TiO<sub>2</sub> carried out with dual rotatable magnetrons and reactive gas control in transition (through the use of a residual gas analyzer [RGA] and high-speed mass flow controllers), resulted in denser films with higher indices than typical sputtered films. However, after correcting for relative power, the deposition rates remain much lower than normal reactive sputtering [24].

Although no production breakthroughs have occurred, work on these unique power supply configurations continues to explore potential to influence and control the deposition conditions of thin films.

### Process Control

From the development of the planar magnetron through the adoption of mid-frequency rotatable magnetrons, the sputtering rate of dielectric materials has been limited by the fundamental shape of the hysteresis curve. The abrupt transitions between a high-rate absorbing metal process and a low-rate transparent dielectric have proven difficult to con-

trol. Much effort continues to be focused on controlling this transition to allow deposition of fully reacted, transparent dielectrics at near metallic rates. The position of various working points for reactive deposition are shown in the hysteresis curve shown in Figure 3 [25].

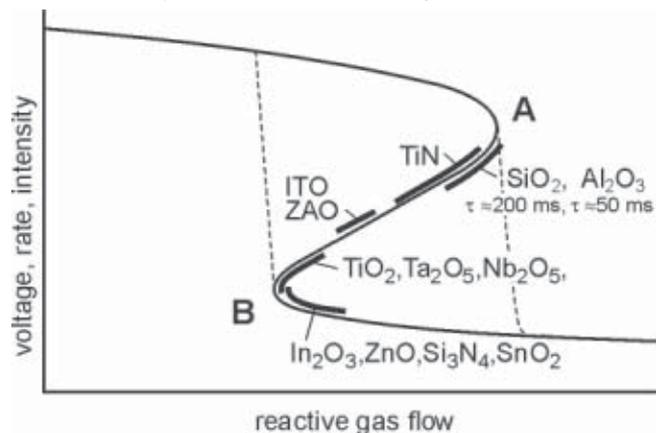


Figure 3. Typical hysteresis curve showing some preferred material working points [25].

One solution has been to sequentially deposit thin metallic films and then react them with an auxiliary plasma. Typically, this is most easily achieved in a multiple pass mode on a rotating drum. Sputtering targets can be run in unpoisoned, high-rate metallic mode. Reaction is supplied by ion beam or microwave plasma [26, 27].

Controlling sputtering from a reactively sputtered target in transition requires a method to monitor the state of the plasma and rapidly feedback corrections to power or gas flow to maintain operation in

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the transition mode. Two general methods have been under intensive investigation.

Direct measurement of the gas species can be done through partial pressure measurements made via an RGA or mass spectrometer. Feedback controls the sputtering gas via fast mass flow controllers. This was demonstrated for  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  with pulsed DC applications. Alternatively, for oxide depositions, oxygen partial pressure can be monitored by the same oxygen sensors used to control emissions in the automotive industry ("lambda probes") [28].

An indirect way to monitor species in the plasma is to monitor the light emitted by excited atoms or ions in the plasma. Plasma emission monitoring (PEM) or optical emission spectrometry has been applied to the control of  $\text{TiO}_2$  deposition from metal targets. Monitoring of Ti emission lines can be used as a feedback control to power supply or gas flow controllers to maintain sputtering in the transition region. (See Figure 4 [29] for a typical configuration utilizing a plasma emission monitor to control deposition of  $\text{TiO}_2$  from two Ti metal targets on a dual rotatable magnetron.) For materials such as  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ , this has been combined with control loops monitoring the target potential as an indicator of where the process is on the hysteresis loop. Combinations of multiple controllers are typically used to ensure process uniformity across large widths. While excellent rates and uniformity have been demonstrated by such systems, their complexity and sensitivity to changes in process conditions such as load factor have limited their adoption in production [29-31].

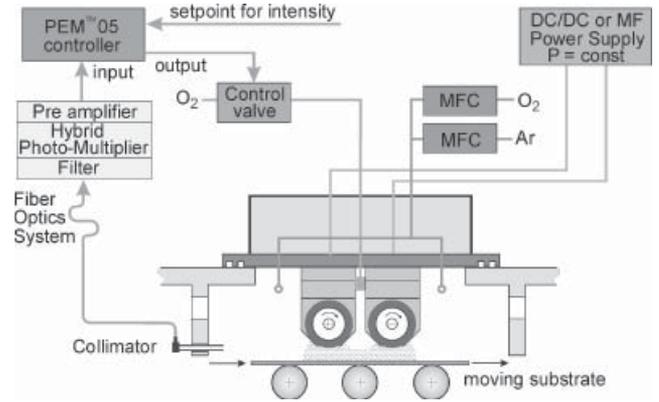


Figure 4. Set up for utilizing PEM to control  $\text{TiO}_2$  process on dual rotating magnetron with mid-frequency power [29].

Efforts to develop robust controls for high-speed reactive sputtering are a continuing focus. Interesting side effects of these activities have included improvements upon the basic Berg model for reactive sputtering, development of modified gas introduction systems to improve response time of gas controls, and other modeling of the impact of deposition source geometry on hysteresis [32, 33].

## Target Material

The development of high-quality target materials for sputtering has always followed in the wake of new magnetron developments. By the mid 1990s plasma spray, vacuum casting, extrusion, and hot isostatic



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pressing technologies were widely applied to the production of new targets for the rotatable magnetron. Conventional planar metal materials (stainless steel, Ag, NiCr, Ti, Sn, Zn, Cr, etc) were all readily available, while Al doped Si provided a reliable source of targets for silicon compounds.

The most interesting new development in the realm of source/target materials is the availability of substoichiometric ceramic materials. Deposition from ceramic targets had been the process of choice for films such as indium tin oxide (ITO) for the display industry for some time. The evaluation of the first ceramic ITO rotatable target was undertaken in 1998 [34]. While ceramic targets are more expensive, processes based on them tend to be more stable and higher rate than comparable reactive sputtering from metallic targets.

For high-rate  $\text{TiO}_2$ , the widespread availability of ceramic targets has become the most direct method for high-rate deposition. Utilizing substoichiometric targets, fully reacted films can be deposited by sputtering in argon with very small additions of oxygen. Deposition rates are comparable or higher than those obtained by reactive sputtering of Ti metal targets in transition with closed loop (PEM or other) process controls. Figure 5 [35] shows the achieved depositions speeds from dual rotatable magnetron ceramic targets. Oxygen levels above 2% typically produce a fully reacted and transparent  $\text{TiO}_2$  film. Process stability and uniformity over long campaigns are much easier to achieve, especially when coupled with mid-frequency sputtering to avoid “disappearing anode” effects.

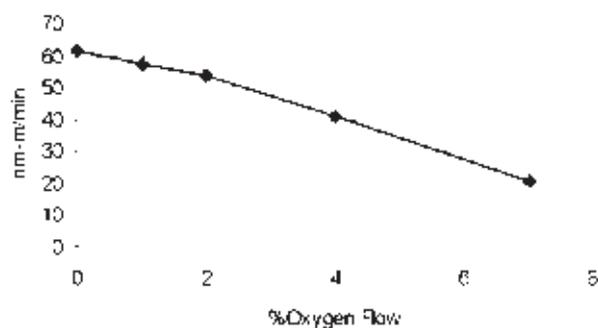


Figure 5. Deposition speed of  $\text{TiO}_x$  from ceramic targets as a function of the  $\text{O}_2$  flow as a % of total gas flow, at 75 kW mid frequency on a 2.9-m target [35].

The ability to sputter in very low oxygen atmospheres offers an unusual advantage to the deposition of low-emissivity films, where great effort is generally made to shield the Ag layer from energetic oxygen bombardment. Deposition of low-E films using all-ceramic targets for single and double low-E films was first shown in 2002 [35].

The higher cost and manufacturing difficulties for rotatable ceramic ITO targets has limited their application. With the growth of the photovoltaic industry, greater interest has come for ceramic Zn:Al oxide (ZAO) targets for lower cost transparent conducting films. Great interest in target manufacturing and performance capability has been shown for ceramic ZAO films. (See the ceramic ZAO target on a rotatable magnetron in Figure 6 [36].) Comparisons of DC, dual DC, and dual mid-frequency sputtering processes from ceramic and metal targets have been widely reported. Effects of target materials and deposition processes on sheet resistance, and more fundamentally, charge carrier density and mobility are areas of ongoing active research. The opportunity for rotatable targets to reduce/minimize process instability caused by nodule growth on planar targets is also of great interest [36-38].

## Substrates

Throughout the history of large area coating, the question of what makes a glass surface “clean enough” for coating has been a difficult one to answer. Some of the mostly highly attended talks in the SVC TechCon Large Area sessions have addressed these issues. The effects of glass storage, aging, water quality, condensation, and separator materials, as well as understanding the mechanisms of glass corrosion are critical to the manufacture of high-quality coatings. Pre- and post-processing of glass can generate stains, glass debris, tin, and organic residues (see Figure 7 [39], from a study of corrosion of stored glass). The development of heat-treatable coatings is reliant on the control of Na diffusion from the glass surface. Baouchi [40] reported on the minimum deposited  $\text{SiO}_2$  thickness required as a good diffusion barrier against Na when heating glass. Duffer [39] spoke to an over-capacity crowd with a detailed survey of the chemistry of glass corrosion and preventative measures. Lingle and Rancourt [41] provided an overall survey of processing impacts on glass and coating quality.

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Figure 6. Ceramic ZAO target on 1 m rotatable magnetron [36].

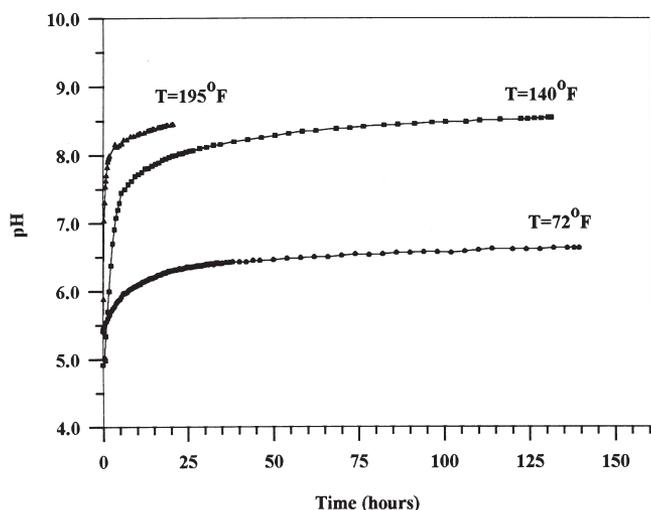
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### Coatings

Two major enabling technologies provided the foundation for the next stage of coating developments. Mid-frequency dual rotatable magnetrons provided a stable, high-rate deposition of  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  for extended production campaigns. This enabled the deposition of materials with much enhanced mechanical and chemical durability and low index materials. High-rate deposition of  $\text{TiO}_2$ , through either plasma emission control or via ceramic targets added a high index material to the inventory of materials with typical moderate indices of 2.0 ( $\text{Si}_3\text{N}_4$ ,  $\text{SnO}_2$ ,  $\text{ZnO}$  and various alloys).

The first  $\text{Si}_3\text{N}_4$ -based low-E coatings were reported based upon DC deposition from dual rotatable cathodes. Low-E stacks based upon all  $\text{Si}_3\text{N}_4$  dielectrics layers exhibited far superior chemical and mechanical durability compared to previous coatings. This enabled much longer storage/transport time and ease of handling by fabricators. However, the requirement to use thick NiCr barriers for adhesion between the Ag and dielectric layers limited the transmission and emissivity perfor-



mance. The use of a  $\text{TiO}_2$  underlayer improved this performance [42].  
*Figure 7. Representation of corrosion mechanisms in pack stored glass. Increase of pH with temperature and time due to hydration [39].*

Within a few years, new families of durable sputtered low-E coatings, with handling performance starting to approach pyrolytic coatings, were commonplace in the industry. These products covered the gamut of single and double silver layer low-E, and low-E “Sun” or solar control and low-E performance [43, 44].

As early as 1995, furnace manufacturers were introducing the concept of a new generation of tempering furnaces specialized for low-emissivity glass. In a conventional furnace based on radiative heating of glass, severe distortion could occur when coated and uncoated surfaces had radically different emissivities (hence absorption of infra-red radiation). A new generation of dedicated low-E furnaces would compensate by the addition of controlled convective heating [45].

Soon, a variety of temperable sputtered coatings were introduced. The ability to sputter, then temper a product eliminated the need to pre-cut glass for tempering prior to coating. As a result, load factor utilization of the coating system could be increased, and response time to provide coated product could be shortened. Low-E stacks were made based upon  $\text{TiO}_2$  layers for improved visible transmission and  $\text{Si}_3\text{N}_4$  layers for durability, handling, and as diffusion barriers. Typically, sub-

stoichiometric NiCr-oxide layers were used as sacrificial barrier layers to protect the silver [46, 47]. Similar approaches were taken to make interference solar control coatings [48, 49].

This period also saw the automotive industry’s on-again/off-again love affair with coating glass. Electrically heated and solar control windshields based on single and double low-E coatings had been introduced in the late 1980s through early 1990s. Through the 1990s, growth in this application was very low. By 2000, a revival of interest in Europe led to a volume of nearly 4 million coated windshields. Though all based upon sputtered low-emissivity coatings, three distinct paths to fabrication were then in use: direct coat on bent windshields, coat flat glass and bend windshields, and direct coat on PET (polyethylene terephthalate) roll coating followed by lamination between two PVB (poly vinyl butyrate) layers. The coated windshield offers multiple capabilities: 7.5% reduction in emissions due to gas savings through reduced air conditioning load, ability to act as antennae, electrically heated defrost/defog. However, after the brief upsurge in adoption from 2000–2002, interest again lagged in the ever cost-sensitive auto industry [50]. Conventional low-emissivity coated glass is now a commodity product, and further development efforts are focused on squeezing the last bits of performance out of the coating designs. Extensive work has been performed to optimize material choice, thickness, and deposition conditions of the protective barrier layers used to protect the Ag from the sputtering plasma during deposition. Analysis of the growth of Ag films has confirmed that a ZnO seed layer provides the best platform for continuous growth of Ag at lower thicknesses, resulting in higher transmission at lower emissivities. The effects of growth conditions, energy inputs, and thickness on the optical constants of the Ag were measured. Models of electron interactions at interfaces for very thin Ag films gave better correlation between sheet resistance and emissivity measurements [51–54].

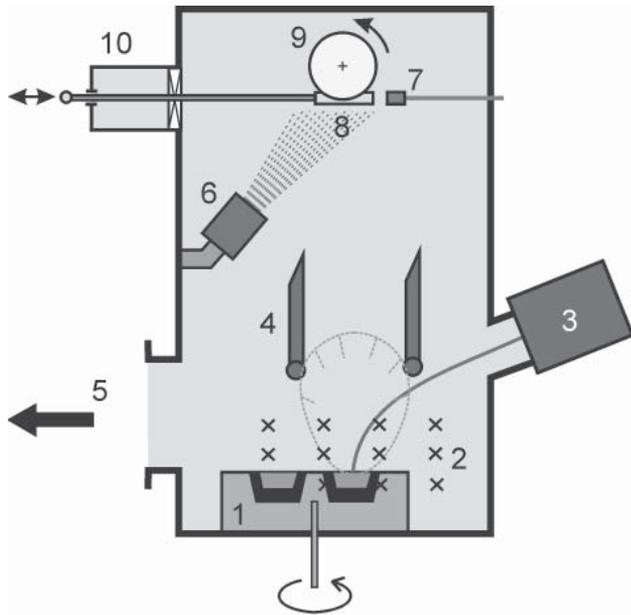
### Electron Beam and Metal Strip Coating

High-rate deposition of extremely thick and dense layers remains a specialized application for ion-assisted electron beam coating. The potential to replace “dirty” protective layers (such as chromates) with more environmentally friendly vacuum coatings has maintained interest in strip metal coating applications. Ion beams have been used for pre-treatment and cleaning and as activation sources for denser films. High-power electron beam guns (>100kW) can provide thick layers of Fe, Cu,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , etc. A design for a system to deposit  $\text{SiO}_2$  on strip steel is shown in Figure 8 [55]. These materials provide functional protective layers, enhanced reflectors, scratch resistance, etc. [55–58].

### The Future

Some of the most interesting areas to emerge in large area coatings have been the realization of large area ion beam sources and the perpetual promise of production of active, switchable coatings. The emergence of new “self-cleaning” coatings and the re-vitalization of the photovoltaic industry also promise broad new areas of application.

Large area ion beam sources have been introduced and evaluated for substrate cleaning, surface modification, ion-assisted deposition of sputtered films, and plasma-enhanced chemical vapor deposition (PECVD) at pressures compatible with sputtering processes. Figure 9 [59] shows a large area linear ion beam source that can also be used for PECVD. Linear ion beam sources act on the same principles as planar magnetrons: a feed gas is introduced into the gap between an anode and cathode. The ionized gas is accelerated by the electric field. A gap in the magnetic cathode provides containment of electrons for enhanced ionization. Inert or reactive gas feed can be used for cleaning, surface enhancement, or ion-assisted deposition. The introduction of organic feedstock allows for deposition by PECVD. Hydrocarbon gases have been used to



- |                     |                      |
|---------------------|----------------------|
| 1 Double crucible   | 6 Ion source         |
| 2 Bending field     | 7 Quartz measurement |
| 3 Axial type EB gun | 8 Substrate carrier  |
| 4 Shutter           | 9 Drum               |
| 5 Pumping           | 10 Load lock         |

Figure 8. Experimental design for  $\text{SiO}_2$  deposition on strip steel [55].

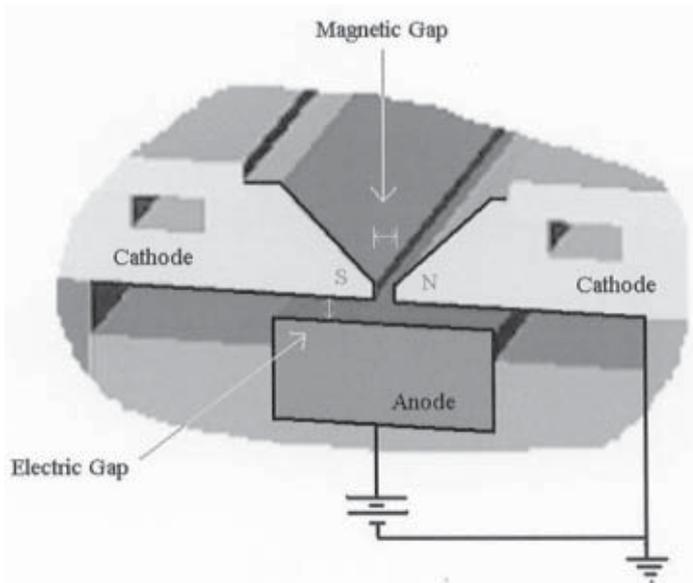
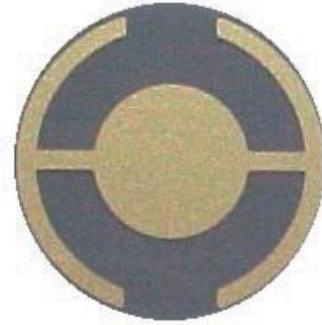


Figure 9. Diagram of Linear Ion beam source and as deposition tool [59].

deposit very hard diamond-like carbon for highly durable protective layers. Sputtering and ion beam deposition have been combined to deposit alternating layers of PECVD and sputtered films for high-durability applications [59].

The potential demand for switchable coatings was shown in a 2002 market study that revealed that the primary end user drivers were durability, reduction in glare and heating, compatibility with low-E coatings, and privacy/light reduction. As we have always seen, the main drawbacks are price sensitivity; while half of the respondents said they would

*continued on page 46*



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## History of Large Area Coatings

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adopt switchable glass if priced at \$11–25/m<sup>2</sup>, this rapidly dropped to 1/6<sup>th</sup> if price was \$26–50/m<sup>2</sup>. By the first half of the decade, competing technologies included conventional absorptive electrochromic, thermotropic, liquid crystal, and metal hydride (reflective transition) coatings. The metal hydride films promised simpler, faster response stacks based on switching hydrogen in and out of the gas phase. As a result of increased interest in switchable coatings, the SVC has dedicated several sessions to “smart coatings.”

The introduction of “self-cleaning” or “low-maintenance” glass based upon either catalytic effects or hydrophobic/hydrophilic coatings was first introduced in atmospheric pressure CVD or pyrolytic processes. This also will be an ongoing area of interest for large area coating manufacturers [60]. The future in economical PV production lies in its transition to industrial large area coating. Going forward, specific areas of overlap, such as large area TCO via Zn:Al oxide will be a continuing focus for large area coatings development.

The history of large area coatings is one of invention, growth, and maturation of a large field of industrial thin film production, with a strong focus on providing products for improved energy efficiency. This focus on energy efficiency took its initial incentive from our first “gas crises” of the early 1970s, but maintained its growth while energy efficiency receded from the public limelight. Thus, as energy efficiency again becomes a primary public issue, there still remains considerable room for future innovation and growth.

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