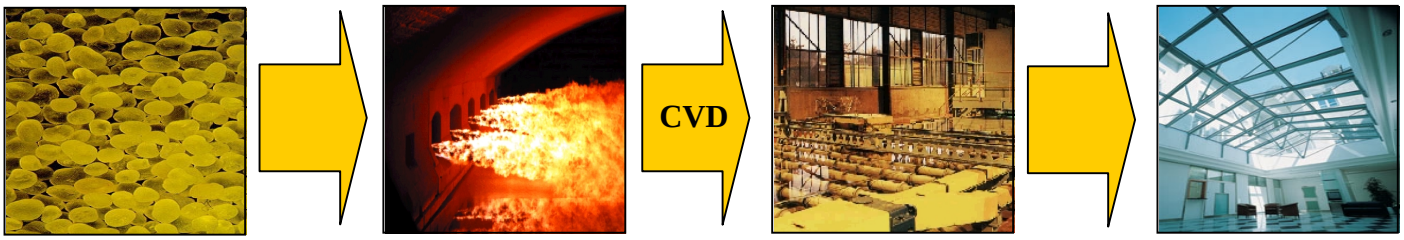
Industrial Materials for the Future R&D Strategies:

A Case Study of Chemical Vapor Deposition (CVD) Methods – Applying Low-E Coatings to Flat Glass for Applications in Sunbelt Locations



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Office of Industrial Technologies
U.S. Department of Energy

October 2002

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List of Acronyms

AIM	Advanced Industrial Materials Program
AL	Air leakage
CVD	Chemical vapor deposition
DMIC	Dimethylindium chloride
DOE	U.S. Department of Energy
HTFR	High-temperature flow reactor
HVAC	Heating, ventilation and air-conditioning
IMF	Industrial Materials for the Future Program
ITO	Indium tin oxide
LOF	Libbey-Owens-Ford
Low-E	Low-emissivity
NREL	National Renewable Energy Laboratory
OIT	Office of Industrial Technologies
R&D	Research and development
SHGC	Solar heat gain coefficient
SNL	Sandia National Laboratory
TMI	Trimethylindium
UV	Ultraviolet
VT	Visible transmittance

1.0 Introduction

This report describes a case study performed by RAND and NREL of government-industry research and development (R&D) aimed at designing new coating methods for the U.S. glass industry. While the project achieved substantial production benefits and energy savings, the impact on the energy efficiency of buildings when the newly developed coatings are installed in windows far outweighs production energy savings.

The R&D described in this report was performed by Sandia National Laboratory (SNL) and sponsored by the Industrial Materials for the Future (IMF) program – the successor to the Advanced Industrial Materials (AIM) program – of the U.S. Department of Energy (DOE) Office of Industrial Technologies (OIT). In addition, a CRADA was established with glass manufacturer and co-sponsor of the R&D project Libbey-Owens-Ford (LOF) to develop new processes at pilot and manufacturing scales.

The principal problem addressed by this effort was developing methods to apply low-emissivity (or low-E) coatings by chemical vapor deposition (CVD). Low-E coatings reduce the thermal transmission through glass in windows. These coatings have been particularly successful in heating-dominated climates, such as those found in the northern U.S., because they reduce heat loss from the window. However, in cooling-dominated climates, such as those found in the southern U.S., low-E coatings made via CVD methods (also referred to as pyrolytic coatings) did not achieve high performance characteristics because they (the coatings) transmitted escalated quantities of solar heat. The next best alternative to a pyrolytic coating is a sputtered coating; however, sputtered coatings must be installed in a double-pane system, which is not typically used in cooling-dominated climates. Thus, there was a lack of high-performance windows to accommodate cooling-dominated climates.

Chemical vapor deposition is a process whereby a gas (the precursor) is dispersed on a layer of molten glass in the production line. The subsequent chemical reactions create a new chemical structure on the surface of the glass, which is the coating.

The R&D team at SNL examined alternate CVD chemistries in an effort to create a low-E coating with reduced solar heat transmittance. In particular, the project R&D team had to determine the stability of a potential precursor gas. Previous examinations of this particular precursor yielded questionable results, which led some to believe that the precursor would be unstable. The R&D team at SNL determined through theoretical calculations, experimental measurement, and numerical simulation that the previously suggested chemistry profile of the precursor gas was incorrect. Under the newly discovered chemistry profile the R&D team determined that the precursor gas would be stable under the service environment.

The R&D team also needed to examine potential reactions that the precursor might undergo with additives used in glass manufacturing and determine if the growth rate would be sufficient to accommodate integration into an on-line float glass coating process.

The chemical vapor deposition methods project resulted in a methodology for developing a CVD process. Coatings produced by this method can be used in cooling-dominated climates to achieve increased energy efficiency. To achieve a reduced solar heat transmittance, the coating blocks the near infrared and ultraviolet portions of the solar spectrum, allowing only primarily visible light to transmit. This is known as a spectrally selective coating. In addition, the pyrolytic coating developed was color neutral, allowing the glass to be used in residential windows.

When the newly developed coatings are installed in windows in cooling-dominated climates our benefits analysis estimates that this technology could save a cumulative 16.7 trillion Btu through 2030.

The balance of this report is organized as follows: Chapter 2 provides a brief overview of the glass industry, explaining why the flat glass sector is critical to energy efficiency. Chapter 3 describes how window performance can be measured and introduces the two primary types of coatings. Chapter 4 briefly outlines the manufacturing processes to apply coatings to glass. Chapter 5 examines the differences between the two primary types of coating with respect to materials properties, benefits and costs to the producer, and benefits and costs to the consumer. Chapter 6 describes the R&D approach that developed a method to apply coatings by CVD. Chapter 7 presents the estimated benefits of using the technologies enabled by the R&D.

2.0 U.S. Glass Industry

2.1 Sectors of the Glass Industry

This report describes a case study performed by RAND and NREL of government funding for research and development aimed at meeting industrial process challenges faced in the flat glass sector of the glass industry. The U.S. glass industry consists of the following five sectors: (1) flat glass (also referred to as float glass), (2) container glass, (3) pressed/blown glass, (4) mineral wool glass and (5) purchased glass products. Table 1 shows these sectors and some of the products manufactured by each sector.[1]

Table 1: U.S. Glass Industry Sectors and Products

Glass Industry				
Flat Glass	**Container Glass**	**Pressed/Blown Glass (specialty)**	**Mineral Wool Glass**	**Purchased Glass Products**
Windows	Beverage containers (beer, wine, liquor, and others)	Cookware	Building batts	Aquariums
Vehicle windshields	Food containers	Light bulbs/tubes	Industrial & appliance insulation	Table tops
Mirrors		Textile fiber	Acoustical insulation	Lab apparatus

Table 2 summarizes statistics associated with each sector of the glass industry. The glass industry has an unfavorable balance of trade due to large imports in the container and specialty (pressed/blown) sectors.

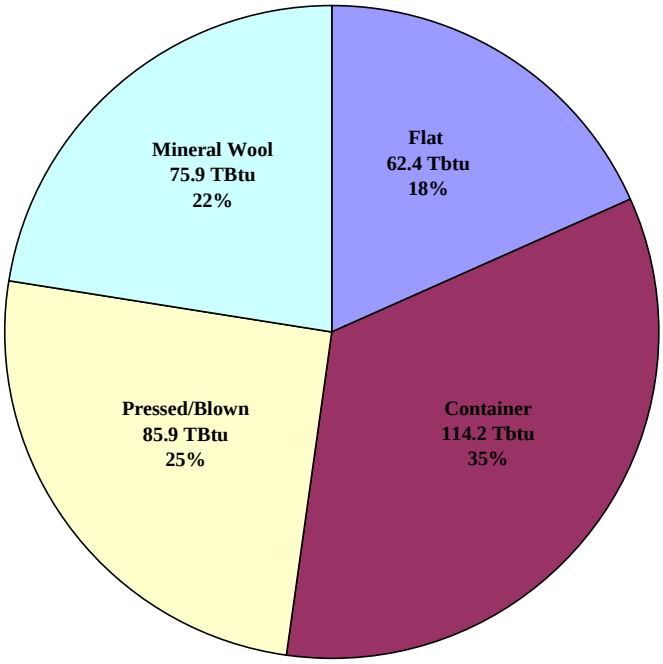
Table 2: Summary of 1999 Glass Industry Statistics[2]

Sector	Shipments ($million)	Production (short tons)	Exports ($million)	Imports ($million)	Establishments	Employees (1000)	Production Wages ($/hr)	Capital Expenses ($million)
Flat	2,746	5,000,521	788	576	36	11,053	21.76	322.7
Container	4,215	9,586,500	174	586	61	19,220	20.05	349.3
Pressed/Blown	5,787	2,484,182	1,298	2,038	515	35,013	15.74	636.8
Mineral Wool	4,844	3,040,000	360	251	298	22,823	17.12	285.8
Purchased Glass Products	10,847	N/A	1,157	1,047	1,657	62,405	12.79	N/A
Industry Total	**28,439**	**20,111,203**	**3,777**	**4,498**	**2,567**	**150,514**	**17.49**	**1,594.6**

The glass industry is one of the nine most energy intensive industries, consuming approximately 340 trillion Btu per year. Figure 1 shows the distribution of energy consumption in the glass industry among the four major sectors.

[1] Energy and Environmental Profile of the U.S. Glass Industry, U.S. Department of Energy, Office of Industrial Technologies, April 2002. Available at: http://www.oit.doe.gov/glass/profile.shtml.
[2] Energy and Environmental Profile of the U.S. Glass Industry, op. cit.

Figure 1: Distribution of Energy Consumption in the U.S. Glass Industry[3]



2.2 Flat Glass Sector

Figure 1 shows that the flat glass sector is the least energy-intensive sector of the U.S. glass industry with respect to energy consumption related to manufacturing. However, the flat glass sector has a large impact on U.S. energy consumption because flat glass is widely used in building structures from residential homes to skyscrapers. Approximately 5% of U.S. energy consumption can be attributed to windows in residential and nonresidential buildings. Additionally, lighting systems account for approximately 5% of U.S. energy consumption.[4] By providing consumers with high-performance windows, the flat glass sector can increase the energy efficiency of buildings.

While the flat glass sector is the least energy-intensive manufacturing sector of the glass industry, it can have a large impact on U.S. energy consumption because its products (windows) play a key role in determining the energy efficiency of buildings.

Consumers have a wide variety of glass products from which to choose, each with different performance characteristics. The type of glass chosen by consumers can strongly influence the energy efficiency of buildings. The performance of a particular type of glass used in a window is dependent on the climate in which the window will be installed. Thus, it is important to first consider the type of climate in which a window will be required to perform before one can determine an ideal suite of performance characteristics. The following section describes how window performance can be measured and how the climate in which the window is used impacts which characteristics are most important to determining the energy efficiency of the window.

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[3] Ibid.

[4] Selkowitz, Stephen. Window Performance and Building Energy Uses, American Institute of Physics Conference Proceedings, Number 135, 1985, ISBN 0-88318-334-X.

3.0 Window Performance and Building Energy Use

Window performance is crucial to a building's energy efficiency. Approximately 30 to 40% of building energy consumption is associated with heating, ventilation and air-conditioning (HVAC) and lighting systems.[5] Selkowitz defines six primary factors that affect window energy performance[6]:

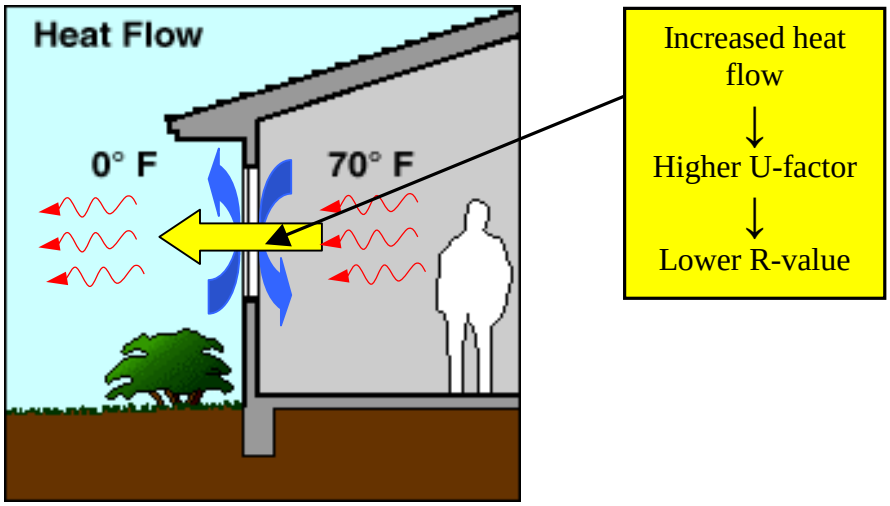
1) Thermal transmission.
2) Light transmission.
3) Control of solar heat gain.
4) Infiltration.
5) Ventilation.
6) Condensation.

Several measurable quantities that determine the energy efficiency of a window are discussed in the following sections.

3.1 U-Factor and R-Value

The U-factor is a measure of rate of thermal heat transfer through a window. As the U-factor decreases, the rate of thermal heat transfer also decreases. It is measured in units of energy per unit of time, area and temperature (e.g. Btu/hr-ft^2-°F). The inverse of the U-factor is known as the R-value. The R-value indicates the insulating value of the window. Thus, as a window transfers less heat, the R-value increases. In colder, heating-dominated climates, the U-factor and the R-value are critical to the energy performance of a window. However, in cooling-dominated climates, the U-factor and the R-value are not as critical.

Figure 2: Thermal Transmission of Windows – U-factor and R-value[7]

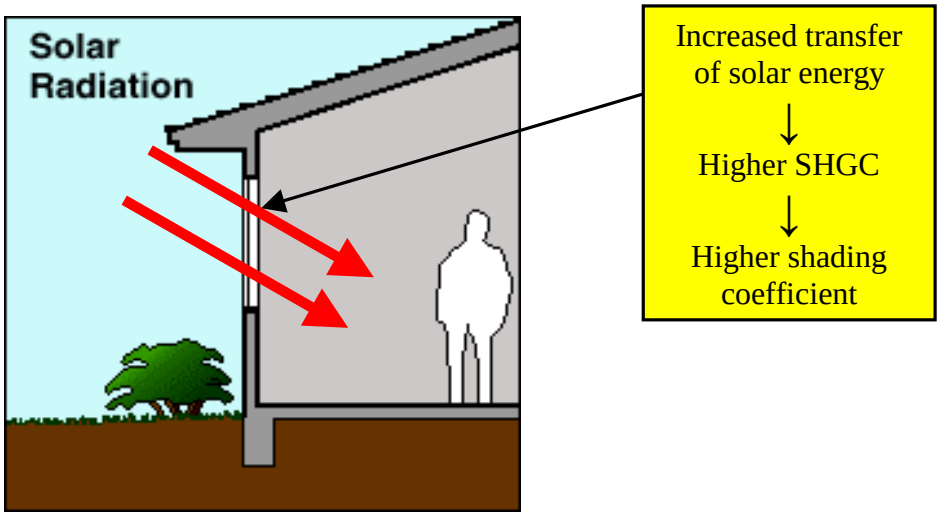


[5] Spectrally Selective Glazings, Federal Technology Alert, August 1998, DOE/EE-0173.
[6] Selkowitz, Stephen. Window Performance and Building Energy Uses, op cit.
[7] Figure taken from Efficient Windows Collaborative. Available at http://www.efficientwindows.org/selection2.html.

3.2 Solar Heat Gain Coefficient (SHGC) and Shading Coefficient

The solar heat gain coefficient is the percentage of the solar energy that enters a building through the window. As the SHGC increases, the amount of heat transfer into the building from sunlight increases. Another quantity used to measure this characteristic of window performance is the shading coefficient. The shading coefficient is a measure of the amount of solar energy transferred through the glass. As the shading coefficient increases, the amount of energy transferred through the window from sunlight increases. The SHGC (or shading coefficient) is the most important characteristic of a window for cooling-dominated climates, such as are found in Sunbelt locations.

Figure 3: Solar Heat Gain of Windows – SHGC[8]

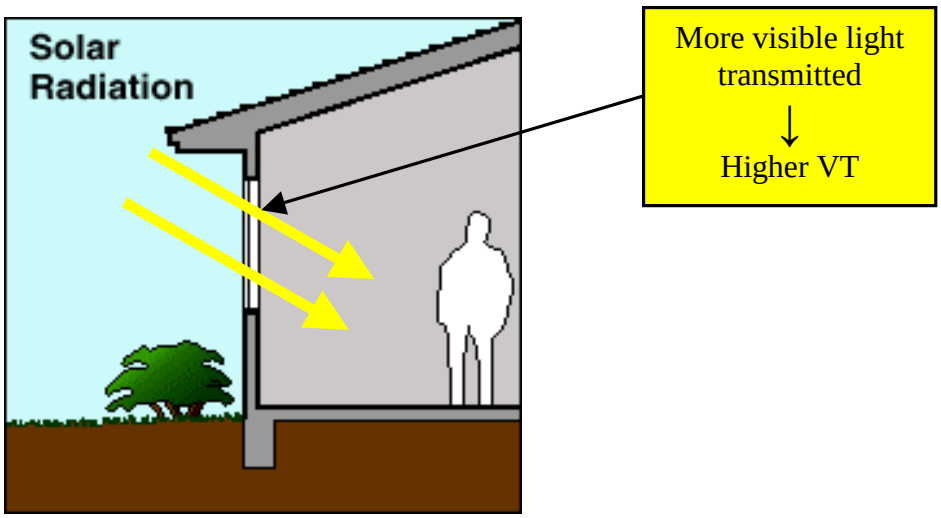


3.3 Visible Transmittance (VT)

Visible transmittance (VT) is a measure of the amount of visible light that is transmitted through a window. As VT increases, the amount of visible light transmitted through the window increases. VT is important when considering the energy efficiency of a building because it can reduce the load on electric lighting systems during the day. As a building has more sunlight transmitted, occupants may not rely as strongly on electric lights, thus reducing energy consumption.

[8] Ibid.

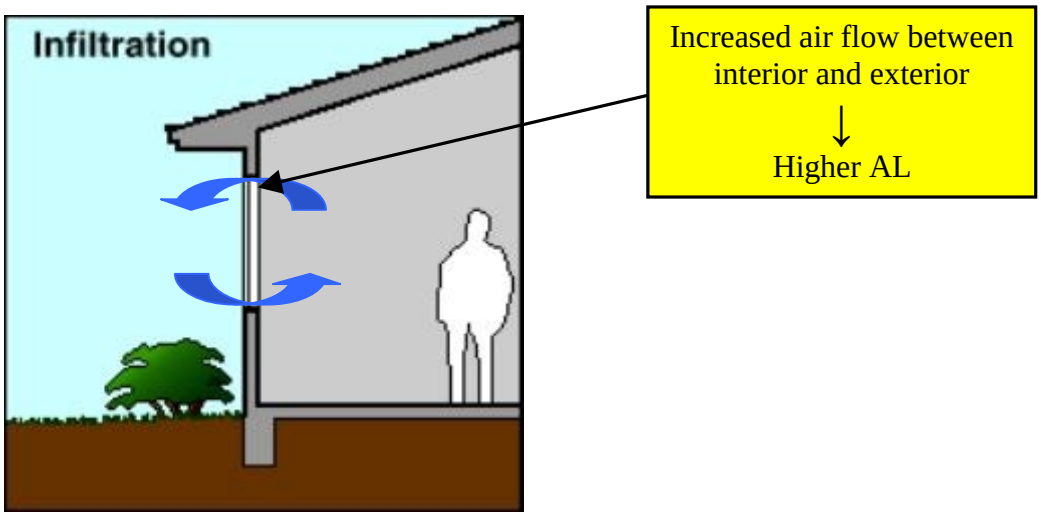
Figure 4: Visible Light Transmittance of Windows – VT[9]



3.4 Air Leakage (AL)

Air leakage (AL) is a measure of the flow rate of air through gaps in the window assembly. As the flow of air between the interior and the exterior increases, the AL increases. AL is measured in volume of air per area of window. Although AL does play a role in the energy performance of a building, it is not as critical as the U-factor or the SHGC.

Figure 5: Air Leakage of Windows – AL[10]



[9] Ibid.
[10] Ibid.

3.5 Designing Windows to Attain a Desired Performance Profile

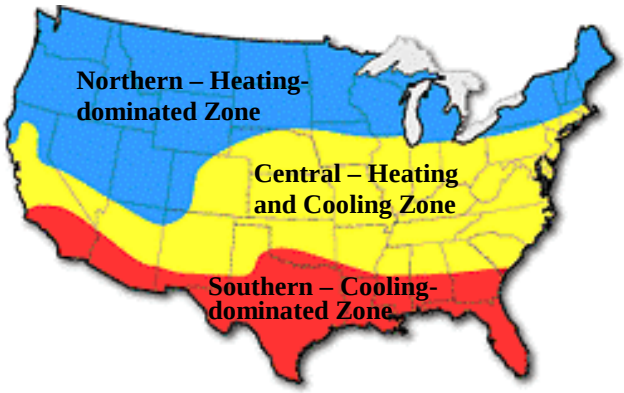
3.5.1 Low-emissivity (Low-E) Coatings on Flat Glass

Glass manufacturers are able to design window systems to achieve a more ideal performance profile in a particular climate. The U-factor and the SHGC are crucial parameters in evaluating the energy efficiency of a window; both characteristics have a direct impact on performance. Visible light transmittance indirectly affects the energy efficiency of a window. An increase in visible light transmittance can reduce energy consumption by providing more daylight, reducing the demand on electric lighting systems.

Glass manufacturers will often use coatings to tailor the performance characteristics of a window. Low-emissivity, also known as low-E, coatings are used primarily to lower the U-factor of a window. Thus, low-E windows act as better thermal insulators between the inside and outside environments. Low-E coatings consist of a thin film that lies on the surface of the glass and changes the optical properties of the glass. They were introduced commercially in 1982 and now account for more than 40% of all residential windows.[11]

The characteristics of low-E coatings make them ideal for use in northern, heating-dominated climates. Low-E coatings reduce the thermal transmission through the window, thus, reducing demand on heating systems. Figure 6 is a map of the continental U.S. showing the different climatic zones.

Figure 6: Climatic Zones of the Continental United States[12]



Before the IMF glass coatings projects, low-E coatings typically had a large SHGC. Thus, low-E coatings could not be used in southern, cooling dominated climates because the window would allow too much solar energy to be transmitted through the window. In cooling-dominated climates – also referred to as "Sunbelt" locations (the southern third

[11] Selkowitz, S.E., et al. Building Technologies Program: 1994 Annual Report, Windows and Daylighting, Energy & Environment Division, Lawrence Berkeley National Laboratory, LBL-36553. Available at http://eande.lbl.gov/BTP/pub/annrep94/annrep94.html.

[12] Figure taken from Efficient Windows Collaborative. Available at http://www.efficientwindows.org/selection2.html.

of the U.S.) – control of solar heat gain is the dominant characteristic that determines energy performance of windows. Decreased solar heat gain lowers the demand on cooling systems.

For cooling-dominated climates, such as Sunbelt locations, low-E coatings can be beneficial if the SHGC can be minimized.

3.5.2 Types of Low-E Coatings

There are two primary techniques used to deposit low-E coatings onto flat glass: (1) batch sputtering and (2) chemical vapor deposition (CVD).

Batch sputtering is the traditional technique used to apply coatings to glass. However, batch-sputtering cannot be used in a single-glaze window system. The majority of windows in cooling-dominated climates use single-glaze windows. Therefore, sputtered coatings do not have extensive applicability in Sunbelt locations.

Low-E coatings applied using CVD methods are often referred to as pyrolytic coatings. Pyrolytic coatings can be used in single-glaze window systems. However, prior to the IMF-funded chemical vapor deposition methods project, pyrolytic coatings had a high SHGC. To overcome this problem, the optical properties of the coatings were tailored such that the near infrared and ultraviolet portions of the solar spectrum are reflected, while the visible portions of the spectrum are transmitted. This arrangement allows for greater transmittance of visible light, while blocking energy-bearing light from the invisible portions of the solar spectrum. Low-E coatings that transmit and block particular portions of the solar spectrum are called spectrally-selective coatings. In addition, to accommodate the broadest range of applications, an ideal coating would be color neutral. Since residential homes typically use color-neutral windows, a coating that is invisible to the naked eye can be applied more broadly.

A result of the IMF-funded chemical vapor deposition methods project was a CVD method to apply pyrolytic coatings to glass for use in Sunbelt locations. To accomplish this end, a pyrolytic coating that has a low SHGC and is color neutral was necessary.

Section 5 will discuss the differences between the coatings mentioned here in more detail. The following section discusses the differences between the batch-sputtering and CVD coating techniques.

4.0 Low-E Coating Deposition Techniques

4.1 Float Glass Process

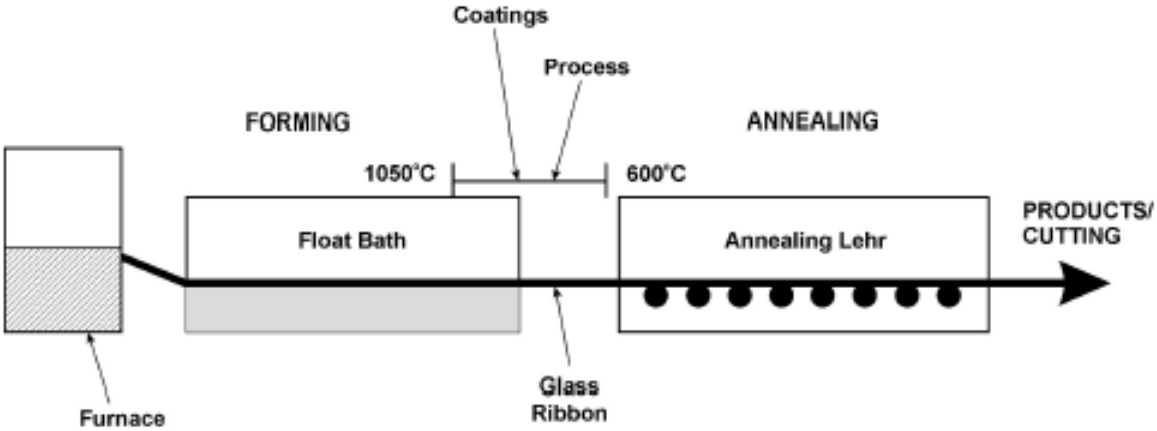
The float glass process was developed by the Pilkington brothers in the 1950s. This process revolutionized the flat glass sector, replacing previous processes that were more energy intensive.[13]

In the float glass process, molten glass at a temperature of approximately 1950°F (1065°C) comes from the furnace and is fed onto a pool of molten tin (sometimes referred to as the float or tin bath). The float bath can be 160 – 190 feet (49 – 58 m) long and 12 – 30 feet (3.7 – 9.1 m) wide. As the molten glass reaches the pool of molten tin, the glass spreads uniformly across the bottom layer of tin. The molten glass then begins to cool while its surface conforms to match that of the uniform molten tin. The result is a glass with a smooth surface of uniform thickness and without distortion. The molten glass exits the float bath at a temperature of approximately 1125°F (600°C).[14]

After exiting the float bath, the molten glass enters the annealing lehr. The annealing lehr is used to relieve any stresses that may have been created on the surface of the glass during forming. After it is annealed, the glass is slowly cooled to room temperature and then cut.[15]

Figure 7 shows a schematic of the float glass process.

Figure 7: Float Glass Process[16]



[13] Energy and Environmental Profile of the U.S. Glass Industry, op cit.
[14] Ibid.
[15] Ibid.
[16] Figure taken from Energy and Environmental Profile of the U.S. Glass Industry, op cit.

4.2 Batch-sputtering Techniques

Coatings applied using batch-sputtering techniques are completed after the glass has come off the production line. Additionally, glass is sputtered-coated after production and after the glass has been tempered and cut into its final form. Thus, batch sputtering is an off-line process. This is the traditional method used to deposit coatings on glass; hence, batch sputtering can be used to apply a wide variety of coatings to glass.

Batch sputtering is performed in a vacuum chamber where an ion beam hits a target. The subsequent reaction causes molecules of the target to fall and deposit on the surface of the glass. Sputtering occurs at low temperatures relative to CVD methods. Sputtered coatings are sometimes referred to as 'soft' coatings because they require special care to assure that the coatings are not damaged during handling.[17]

4.3 Chemical Vapor Deposition (CVD) Techniques

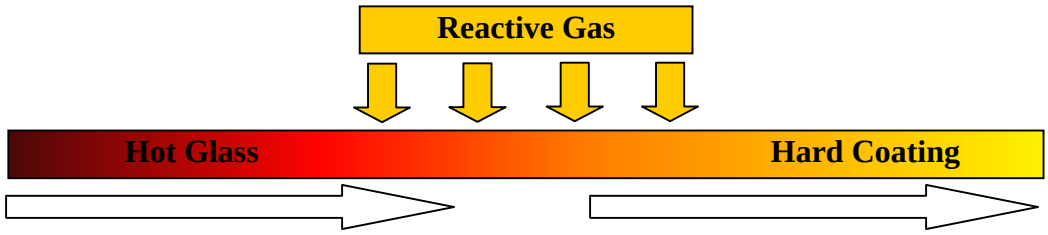
Coatings applied using chemical vapor deposition (CVD) techniques are produced during the float glass process on the float glass line. Hence, applying coatings by CVD is an on-line process. CVD methods can be employed in the float glass process in three locations:

(1) in the float bath (750 – 600°C),
(2) in between the float bath and the annealing lehr (600 – 570°C), or
(3) in the annealing lehr, after the annealing zone (<500°C).[18]

Coatings applied using CVD methods are commonly referred to as pyrolytic coatings. CVD methods involve reacting a precursor gas with the hot surface of the glass on the float line. As a result of this chemical reaction, the surface of the glass takes on a new chemical structure. This coating is sometimes referred to as a 'hard' coating because the coating becomes part of the surface of the glass and is thus more durable than sputtered coatings. The reactions must occur very quickly to avoid slowing down the float line. A line carrying a twelve-foot wide ribbon of glass might move at approximately one foot per second.[19] In addition, the CVD process must be integrated into the float line without disrupting the float glass process. Figure 8 shows a schematic of the CVD process.

The following section discusses the differences between pyrolytic and sputtered coatings.

Figure 8: Chemical Vapor Deposition Process



[17] Coatings on Glass: Technology Roadmap Workshop (September 2000), Sandia National Laboratories, Livermore, CA. Available at: http://www.ca.sandia.gov/CRF/03_Reports/04_GlassCoatings/.
[18] McCurdy, Richard J. Successful Implementation Methods of Atmospheric CVD on a Glass Manufacturing Line, *Thin Solid Films*, vol. 351 (1999) pp. 66 – 72.
[19] Coatings on Glass: Technology Roadmap Workshop, op cit.

5.0 Comparison of Pyrolytic (CVD) and Sputtered Coatings

Low-emissivity (low-E) coatings are applied flat glass to in architectural applications to reduce the amount of solar heat transmitted through windows. Differences between pyrolytic and sputtered coatings can be separated into three distinct categories as follows:

1) Materials properties
2) Production benefits and costs
3) Consumer benefits and costs

5.1 Materials Properties

5.1.1 Materials Properties of Sputtered Coatings

Sputtered glass is produced by depositing silver and oxide multi-layers onto the glass after production. Sputtered coatings are applied at low temperatures as compared to pyrolytic coatings (produced by CVD). Thus, sputtered coatings are multiple layers (typically 9 – 12 layers) of metal oxides adhering to the surface of the glass.

5.1.2 Materials Properties of Pyrolytic Coatings

Pyrolytic coatings are produced using the chemical vapor deposition (CVD) method, whereby metal oxides are deposited onto the surface of the glass during production while the glass is still in a molten state. Pyrolytic coatings are applied to molten glass at temperatures of approximately 600 - 700°C.[20] Thus, pyrolytic coatings become part of the glass, rather than a layer deposited on the glass surface.

5.2 Production Benefits and Costs

5.2.1 Production Benefits and Costs of Sputtered Coatings[21]

Sputtered coatings are applied off-line in a vacuum chamber by hitting a target metal with an ion beam to deposit the resultant ions onto the glass, forming a thin film. Coatings are applied in multiple layers. Batch-sputtering techniques offer several benefits:

(1) Batch sputtering is the traditional technique used to deposit coatings on glass; thus, there is a well-established understanding of a wide variety of candidate materials that can be used to form a coating.
(2) Processes necessary to apply and handle coatings are well-established.
(3) Performance properties of sputtered glass are superior to pyrolytic glass (produced using CVD) for many applications.

There are several drawbacks of applying coatings using sputtering techniques:

(1) Applying coatings off-line requires additional processes and time. In addition, coatings must be deposited in a vacuum chamber.
(2) Since the coating is applied as a layer on top of the glass, sputtered glass requires special handling to avoid scratches before installation, thus, promoting longer lead times. The scratch susceptibility of sputtered glass has caused some to refer to it as 'soft coated.'

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[20] Coatings on Glass: Technology Roadmap Workshop, op cit.

[21] Gore, Paul (Pilkington North America, Toledo, OH). Pyrolytic low-E = Sputtered low-E? Different Process = Different Benefits. Viewed on September 17, 2002 at http://www.doorandwindowmaker.com/fall%202000/pyrolytic%20low-E.htm.

(3) Sputtered coatings tend to be more sensitive to moisture in the air. This factor limits a sputtered coating's shelf life. Therefore, producers must carefully consider the length of time between sputtering and installation to avoid loss of stocks. Once installed, however, the coating is insulated, in a double pane, from damage due to moisture. Thus, glass may not be sputtered until the consumer has placed an order for the glass, promoting longer lead times.
(4) Not all sputtered glass can be tempered. Those that can be tempered cannot be tempered under normal tempering conditions. In addition, annealed and tempered glass used in the same application may display differences in appearance.
(5) Most manufacturers of sputtered glass suggest that coatings on the edge of the glass be deleted. This creates additional processes, requiring time and equipment.

5.2.2 Production Benefits and Costs of Pyrolytic Coatings[22, 23]

Pyrolytic coatings are produced by applying the coating via chemical vapor deposition (CVD). This process is done on the production line, when semi-molten glass is exiting the float /tin bath. As the semi-molten glass comes off the float/tin bath, a chemical vapor is sprayed onto the surface of the glass. A chemical reaction occurs between the vapor and the glass surface, changing the chemical composition of the glass surface, resulting in a coating that strongly adheres to the glass.

Application of coatings by CVD offers several benefits:

(1) Since the deposition of coatings is done on-line, CVD offers excellent lead times.
(2) The coatings become a part of the glass, rather than a layer on the surface of the glass, increasing their resistance to scratches. This eliminates the need for special handling and thus decreases lead times. The scratch resistance of pyrolytic coatings has caused some to refer to it as 'hard coated.'
(3) Coatings have an unlimited shelf life.
(4) CVD is done at atmospheric pressure.
(5) Coatings applied using CVD are stable to tempering.
(6) There is a consistent appearance between annealed and tempered glass used in the same application.

While possessing several benefits from a production viewpoint, CVD is not as widely used as sputtering for the following reasons:

(1) Performance properties of the finished product are not as beneficial as sputtered coatings in many applications.
(2) Coatings must be thickness insensitive so that variations will not result in differences in appearance.
(3) Deposition reactions must occur very quickly (1-2 s) to be applied on the processing line (which moves at approximately 25 cm/s).

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[22] Allendorf, M.D., On-line Deposition of Oxides on Flat Glass, The Electrochemical Society **Interface**, Summer 2001. Available at: http://www.electrochem.org/publications/interface/summer2001/IF6-01-Pages34-38.pdf.
[23] Gore, Paul, op cit.

(4) Since CVD is still maturing as a glass coating process, information on types of chemistries that can be used is limited. This constrains the producer's flexibility in choosing chemistries based on stability of the chemicals in delivery lines, uniform dispersion of the reactants on the glass in the float line, and versatility of deposition equipment to facilitate different chemistries.
(5) Coatings must be uniform and defect-free.

5.3 Consumer Benefits and Costs

5.3.1 Consumer Benefits and Costs of Sputtered Coatings

Sputtered coatings offer a more desirable suite of performance properties for some applications. The solar heat gain coefficient of sputtered glass has the potential to be substantially lower than that of pyrolytic glass. Thus, sputtered glass can act as a better insulator against solar energy than pyrolytic glass.

5.3.2 Consumer Benefits and Costs of Pyrolytic Coatings

Pyrolytic coatings can outperform sputtered coatings in northern (heating-dominated) climates, where solar heat gain is not as critical. The results of the IMF-funded chemical vapor deposition methods project provided glass manufacturers with knowledge of new CVD chemistries that could be used to deposit coatings onto glass. The new pyrolytic coatings yielded glass that is suitable for applications in southern (cooling-dominated) climates. These coatings have substantially reduced solar heat gain coefficients and are thus particularly applicable to southern climates. Sputtered coatings cannot be applied in the single-glaze window system used by the majority of buildings and residences in southern climates.

Before the introduction of these coatings, the only option for consumers in cooling-dominated climates was to use tinted glass. Residential homes, in particular, were not inclined to use tinted glass because of adverse visual aesthetics (i.e. a colored glass). The new coatings allowed consumers to use windows that combined ideal performance properties and aesthetics. The reduced solar heat gain decreases energy used for cooling. In addition, the increased visible light transmission of the new coatings decreases the demand on lighting systems.

Figure 9 summarizes the differences between pyrolytic and sputtered coatings.

Figure 9: Differences Between Benefits and Costs of Pyrolytic and Sputtered Coatings

Low-E coatings

Pyrolytic Coatings (Hard coatings)

Materials Properties

- Deposited using CVD methods
- Deposited at higher temperatures
- Coating becomes part of glass

Production Benefits and Costs

+ On-line CVD processing
+ Excellent lead times
+ High durability
+ Unlimited Shelf life
+ Process done at atmospheric pressure
+ Stable to tempering
+ Consistent appearance between annealed and tempered glass

– Performance properties are not as good as sputtered coatings for certain applications
– Coatings must be thickness insensitive
– Requires fast deposition rate
– Process is an emerging technology
– Coatings must be uniform and defect-free

Consumer Benefits and Costs

+ Outperform sputtered coatings in heating dominated climates (north)
+ Can be used in a single-pane, single-glaze window
+ New CVD methods developed by an IMF-funded project allowed pyrolytic coating to be created that substantially lowered the SHGC → allows pyrolytic glass to be used in cooling-dominated climates (south)
+ High visible light transmittance reduces load on lighting systems

Sputter-coated glass (soft coated)

Materials Properties

- Deposited using batch-sputtering techniques
- Deposited at lower temperatures
- Adheres multiple layers of metal oxides to glass

Production Benefits and Costs

+ Traditional technique used to apply coatings
+ Wide variety of candidate materials that can be used to form coatings
+ Well established processes
+ Performance properties for certain applications are better than pyrolytic coatings

– Off-line processing
– Increased lead times necessary
– Special handling required to avoid scratches
– Sensitive to moisture before installation
– Tempering can cause differences with annealed glass
– Edge deletion is necessary

Consumer Benefits and Costs

+ Superior performance properties in heating-dominated climates (north)
+ Lower SHGC than pyrolytic

– Cannot be used in a single-pane or single-glaze window
– Typically residential windows in cooling-dominated climates (south) are single-pane, single-glaze windows → sputtered coating not used in southern climates

6.0 Description of R&D on CVD Methods for Applying Pyrolytic (Low-E) Coatings to Glass

Chemical vapor deposition (CVD) is the most economical method currently available to deposit coatings on flat glass.[24] CVD can be used to deposit Low-E coatings to improve the energy efficiency of float glass. Potentially useful thin films include tin oxide, indium-doped tin oxide and titanium nitride.

As discussed in the previous section, pyrolytic coatings applied by CVD methods offer a suite of performance properties that allow pyrolytic coatings to be used in cooling-dominated (southern) climates. The use of an indium tin oxide (ITO) film on glass significantly attenuates light in the near infrared region of the solar spectrum. However, an ITO film allows light in the visible spectrum to be transmitted through the glass.[25] Ultraviolet (UV) and infrared light transmittance is critical to the energy performance of windows. Approximately half of the thermal energy in sunlight comes from UV and infrared light. Thus, limiting transmission in this region of the spectrum reduces solar heat gain without reducing visible light transmittance.[26]

Figure 10 shows a representative sketch of the solar spectrum and how an ideal low-E coating might react through each portion of the spectrum. The top portion of the figure describes the type of light in each part of the spectrum (near infrared, visible, and ultraviolet). The graph in this figure displays the solar spectrum as a dotted line. The dashed line and the dark solid line represent the optical properties of an ideal low-E coating with respect to reflectance and transmittance, respectively, through each portion of the spectrum. The light grey solid line represents the light visible through each portion of the spectrum for an ideal low-E coating. *The key idea represented in this graph is an ideal low-E reflects light that is not in the visible spectrum and transmits light that is in the visible spectrum.*

The characteristics of the pyrolytic coatings, enabled by the IMF-funded project, resulted in a window that has: (1) color neutrality, (2) high visible light transmittance, and (3) low near infrared light transmittance. Thus, the knowledge generated by the IMF-funded R&D program enabled a pyrolytic coating to be applied to windows used in residential buildings in cooling-dominated climates.

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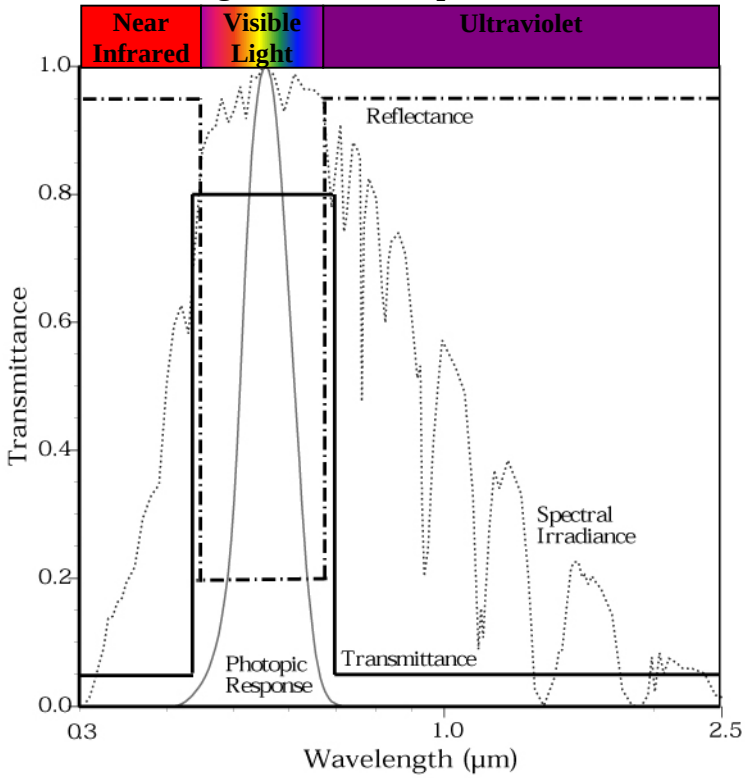
[24] Sandia National Laboratories, Combustion Research Facility News, Flow-reactor experiments and theory shed light on CVD chemistry, November/December 1998, vol. 20, no. 6. Available at: http://www.ca.sandia.gov/CRF/news_pdf/CRFV20N6.pdf.

[25] McCurdy, Richard J. *Thin Solid Films*, op cit.

[26] Selkowitz, S. and E.S. Lee. Advanced Fenestration Systems for Improved Daylight Performance, *Daylighting '98 Conference Proceedings*, (1998) Building Technologies Department, Lawrence Berkeley National Laboratory. LBNL-41461. Available at: http://eetd.lbl.gov/btp/papers/41461.pdf.

Figure 10: Solar Spectrum[27]



To develop CVD methods to apply pyrolytic coatings involving ITO on glass several challenges associated with the high-temperature chemistry of ITO precursors had to be met by the R&D group:[28]

1) Storage issues:
   - Long-term precursor stability
2) Gas-phase kinetics:
   - Deposition rates
   - Reaction of precursors during mixing
3) Reaction byproducts:
   - Waste cleanup

The research results in these areas are summarized below.

6.1 Storage Issues – Long-term Precursor Stability

Bond energies of indium-containing precursors are a critical factor in determining the stability of a precursor during storage and transport. The IMF-funded CVD project first performed theoretical calculations of the bond energies of indium-containing precursors and then measured the bond energy of one potential precursor experimentally. Previous investigations suggested that the indium-containing precursor was not stable enough to be

[27] Figure taken from http://gaia.lbl.gov/hpbf/picture/p11fig1copy.jpg.
[28] Allendorf, M.D., Sandia National Laboratories, presentation at the 2000 Annual Review Meeting for the Industrial Materials for the Future Program, unpublished.

stored or transported in heated lines because the bond energy was measured and determined to be too low. The IMF-funded CVD project determined that all previously reported values for the bond energy were substantially underestimated.[29]

6.1.1 Theoretical Calculations of Indium Compound Bond Energies

To develop a model of industrial coating chemistries, SNL first needed to obtain accurate thermodynamic data for the precursor compounds. These data consisted of molecular heats of formation, heat capacities, and entropies. Indium-containing precursors are used to create an ITO coating. Trimethylindium (TMI) is a useful precursor to create ITO. Thermodynamic data for indium-containing compounds was not well documented in the literature. Clark and Price measured the In-C bond energy to be 47.2 kcal mol^{-1}. Theoretical values of the In-C bond energy were calculated by SNL using a fourth order Möller-Plesset perturbation theory and databases (Stevens/Basch/Krauss/Jasien/Cundari-21G ECP Basis (SBKJC+ECP)) for indium. The accuracy of these databases has not been tested. This method calculated the In-C bond energy to be roughly 65.3 kcal mol^{-1}. While there is considerable uncertainty in this value, it suggests a significantly stronger In-C bond energy than was generally reported in the literature. Based on previous experience predicting bond energies for other main-group compounds, The SNL R&D team asserted that the previously calculated values for the In-C bond represented an underestimate.[30]

A second method was used to predict the In-C bond energy to verify the values arrived at using the fourth order Möller-Plesset perturbation theory and the SBKJC+ECP databases. The bond energies for lighter Group-III compounds were examined; see Table 3. G2 calculations were performed to determine the heat of formation. G2 calculations are generally accepted to be in reasonable agreement with available data. The data in Table 3 suggest the following three characteristics of Group III bond energies[31]:

1) M-C bonds (where M = B, Al or Ga) decrease in strength from the first to the third row of the periodic table of elements. This suggests that the bond energy for In-C would be at least 68 kcal mol^{-1} (In is in the fourth row below Ga).
2) The M-C bond energy is not dependent on the number of methyl radicals. M-Cl bonds decrease with each M-Cl bond.
3) From the first to third row, M-OH bonds decrease in strength more rapidly than M-C bonds. The data suggests that the In-C bond energy will be greater than the In-OH bond energy.
4) The In-C bond energy will likely be less than the In-Cl bond energy. This suggests that reactions are more likely to occur with HCl, rather than H_2O or O_2.

[29] McDaniel, Anthony H. and Mark D. Allendorf, Autocatalytic Behavior of Trimethylindium during Thermal Decomposition, *Chemistry of Materials*, (2000) Vol. 12, No. 2, pp. 450 – 460.
[30] U.S. Department of Energy, Advanced Industrial Materials (AIM) Program: Compilation of Project Summaries and Significant Accomplishments FY1998 (May 1999), Oak Ridge National Laboratory, ORNL/TM-1999/84. Available from the National Technical Information Service, Springfield, VA, http://www.ntis.gov/ordering.htm.
[31] Ibid.

Table 3: Bond Energies in Group-III Compounds (kcal mol^{-1})

Species	M-C	M-Cl	M-OH
BCl_3		118.1	
$B(CH_3)_3$	103.9		
$AlCl_3$		117.8	
$AlCl_2(CH_3)$	86.1	121.9	
$AlCl(CH_3)_2$	84.5	124.9	
$Al(CH_3)_3$	84.2		
$Al(OH)_3$			130.3
$Al(OH)_2CH_3$			
$Al(OH)(CH_3)_2$			132.3
$GaCl_3$		100.4	
$GaCl_2(CH_3)$	76.2	105.7	
$GaCl(CH_3)_2$	75.8	112.2	
$Ga(CH_3)_3$	76.3		
$Ga(OH)_3$			79.0
$Ga(OH)_2CH_3$	78.5		76.6
$Ga(OH)(CH_3)_2$	77.6		73.6
$Ga(OH)(CH_3)Cl$	77.9	112.0	71.7
$Ga(OH)Cl_2$		104.6	69.0
$Ga(OH)_2Cl$		109.9	73.9

The results of both approaches to estimating the heat of formation of indium-containing compounds suggest that the values traditionally referred to in the literature are significantly underestimated.

6.1.2 Empirical Measurement of Indium Compound Bond Energies

Experiments were performed to (1) verify the calculated bond energies, (2) verify that indium-methyl compounds are stable under storage conditions, (3) measure degradation during transportation and (4) measure reaction rates with other compounds that might be present in the service environment (such as HCl).

Experiments were performed using SNL's high-temperature flow reactor (HTFR). All studies that previously sought to measure the In-C bond energies in TMI used an HTFR. However, previous experiments relied on two key assumptions: (1) the decomposition of TMI is entirely homogeneous and occurs by the sequential loss of methyl ligands as shown by the following reactions:

$$In(CH_3)_3 \leftrightarrow In(CH_3)_2 + CH_3 \quad (1)$$
$$In(CH_3)_2 \leftrightarrow InCH_3 + CH_3 \quad (2)$$
$$InCH_3 \leftrightarrow In + CH_3 \quad (3)$$

and (2) these reactions are rate limiting below a particular temperature. Thus, the activation barrier for reaction 1 was presumed to be the In-C bond energy.[32] The R&D

[32] McDaniel, Anthony H. and Mark D. Allendorf, Autocatalytic Behavior of Trimethylindium during Thermal Decomposition, op cit.

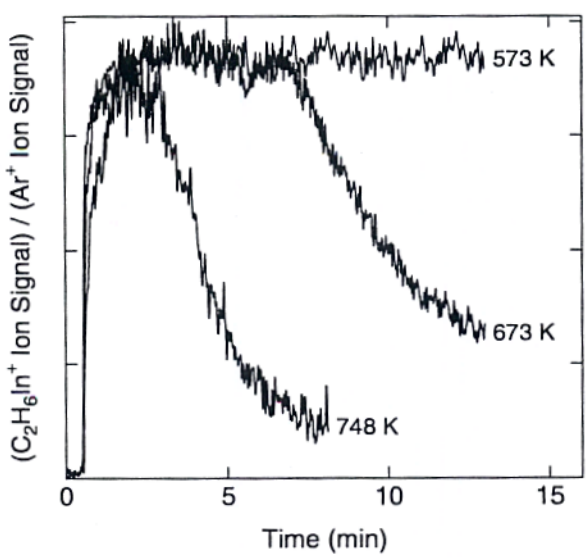
team for the IMF-funded chemical vapor deposition methods project at Sandia National Laboratories (SNL) called these assumptions into question for several reasons:

(1) A heterogeneous decomposition of TMI might explain why previous investigators had large uncertainties in their experiments.
(2) Previous experiments did not obtain repeatable results, unless the HTFR tube walls were cleaned sufficiently of all deposits that formed during the experiment.
(3) Carrier-gas effects may have hindered the accurate measurement of the activation energies.
(4) Theoretical calculations suggest that the In-C bond energy might be significantly greater than previously reported.[33]

The results of the experiments suggested that TMI is stable at elevated temperatures; however, it experiences an autocatalytic reaction with the hot surfaces of the reactor. There is a short induction period when TMI does not decompose under conditions that would require decomposition based on previous reports. When deposits, which are quite reactive with TMI, form in sufficient quantity, TMI begins to decompose. Therefore, elevated temperatures are not responsible for the decomposition of TMI, but rather the autocatalytic reaction leads to decomposition.[34]

Figures 11 shows the results of the HTFR experiments examining the potential decomposition of TMI at three different temperatures (573 K, 673 K, and 748 K) and are discussed below.

Figure 11: TMI Presence vs. Time for Various Temperatures[35]



[33] Ibid.
[34] Ibid.
[35] Figure taken from U.S. Department of Energy, Advanced Industrial Materials (AIM) Program: Compilation of Project Summaries and Significant Accomplishments FY1998, op cit.

In these experiments, TMI was introduced into the reactor at 0.5 minutes, at 15 Torr with a 0.3 second residence time. It is evident from the figure that at 573 K TMI is in an unreactive, stable state. At 673 K, TMI experiences a short induction period of approximately 5 minutes. Then it begins to decompose until approximately 60% of the TMI has decomposed at which point it levels off (~14 minutes). At 748 K, TMI begins to decompose almost immediately and quickly decomposes almost completely.[36, 37]

Subsequent experimentation and examination of the HTFR tubes revealed that deposits formed on the inner surface of the tubes. These deposits are believed to be of the form CH_xIn (x = 1, 2, 3) and In. The deposits were identified by reacting them with HCl under elevated temperatures.[38]

The results of HTFR experiments suggest that the decomposition of TMI is heterogeneous, not homogeneous. Numerical modeling and theoretical calculations of the chemistries involved suggest that the reaction is heterogeneous and the bond energy of In-C is greater than previously believed. The significance of this finding on the prospect of using indium-containing precursors in an industrial CVD glass coating process is that the indium-containing compounds appear to be stable enough to avoid decomposition during storage and transportation in heated lines.[39] The lower boundary for the bond energy was estimated based on experiments and theoretical calculations to be 58 kcal mol^{-1}.[40]

6.2 Gas-phase Kinetics

6.2.1 Deposition Rate of Indium-containing Precursors

Typical coating thickness is in the range of 100 – 5000 Å. At float line speeds of approximately 1 ft/s, deposition rates can be required up to approximately 2000 Å/s. In addition, the precursor reaction with the glass surface must be uniformly distributed over the area of the glass. The reaction must also be sufficiently slow enough to avoid completion in the delivery line or in the nozzle where it is eventually dispersed over the molten glass.[41]

Organotin halides are commonly used as precursors for CVD because of their high deposition rates. Some glass manufacturers use precursors such as dimethylindium chloride (DMIC) for deposition of ITO for this reason.[42]

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[36] Ibid.
[37] U.S. Department of Energy, Advanced Industrial Materials (AIM) Program: Compilation of Project Summaries and Significant Accomplishments FY1998, op cit.
[38] McDaniel, Anthony H. and Mark D. Allendorf, Autocatalytic Behavior of Trimethylindium during Thermal Decomposition, op cit.
[39] Ibid.
[40] U.S. Department of Energy, Advanced Industrial Materials (AIM) Program: Compilation of Project Summaries and Significant Accomplishments FY1998, op cit.
[41] McCurdy, Richard J. Successful Implementation Methods of Atmospheric CVD on a Glass Manufacturing Line, op cit.
[42] Ibid.

6.2.2 Reaction of Precursors during Mixing

Hydrogen chloride (HCl) is sometimes used as an additive by manufacturers in the glass coating process. The IMF-funded chemical vapor deposition methods project determined that TMI reacts quite rapidly with HCl. The result produces dimethylindium chloride (DMIC) and methane by the following reaction:

$$In(CH_3)_3 + HCl \rightarrow (CH_3)_2InCl + CH_4 \qquad (4)$$

At a temperature of 348 K, reaction 4 goes to completion in 500 ms. Since DMIC is also a useful precursor, this reaction could be used to generate DMIC. Subsequent reaction of DMIC with HCl could condense and clog the delivery lines. However, this reaction is much slower and is therefore not considered a problem.[43]

6.3 Reaction Byproducts – Waste Cleanup

The CVD process is performed in an enclosed area with inlet and outlet vents to control the flow of reaction byproducts. As noted by McCurdy, "Exhaust gas byproduct treatment for such a large scale process is always a concern. Commonly if the exhaust gases contain chlorine, wet scrubbing techniques with a conventional filter press are normally sufficient. For effluent gases that are not easily reacted or wetted by aqueous solutions, incineration is the primary option. Here the precursor gases are transformed into their solid oxides and collected."[44]

The following section describes the potential energy savings of the IMF-funded chemical vapor deposition methods project.

[43] U.S. Department of Energy, Advanced Industrial Materials (AIM) Program: Compilation of Project Summaries and Significant Accomplishments FY1998, op cit.

[44] McCurdy, Richard J., et al. Design and Integration of High Volume Multilayer CVD System on a Float Glass Manufacturing Line, *Electrochemical Society Proceedings,* Vol. 96-5, pp. 484 – 489.

7.0 Benefits Analysis – Advanced Manufacturing Using Chemical Vapor Deposition Technology for e-Windows Coatings

This analysis estimates the annual and cumulative energy savings for the Industrial Materials for the Future (IMF) program research in advanced manufacturing methods using chemical vapor deposition (CVD) technology for applying solar reflective coatings on glass for residential buildings.

One manufacturer in the industry, producing e-Windows applicable to the southern climate zone, has adopted the technology developed by the IMF program. The new technology now makes it economic to apply and sell solar reflective coatings to compete with clear single-pane windows. This manufacturer now faces competition from two other manufacturers, neither of whom at the moment has an equivalent product.

Besides the energy savings, the new advanced process produces energy and other savings in the production of CVD films. The new technology allows for continuous deposition of the e-film at high glass processing temperatures instead of batch process at lower temperatures. The new process also produces a coated window with a shelf life of one to one-and-a-half years. The longer shelf life eliminates the need to batch order the window coating (which currently has a shelf life of two to seven days). This allows for energy and cost savings throughout the supply/distribution chain, allows for increased competition due to lower entry barriers for downstream suppliers in the chain, and promotes lower prices for the product.

The above savings are not estimated in this analysis due to the current proprietary information of the lead manufacturer who developed the process. Instead, the benefits estimates for this analysis concentrates on the energy savings of the e-glass in residential window applications – the major market for the new technology.

e-Windows technology research was initiated in 1976 and saw its first commercial applications in 1981. Since then the technology has penetrated about 30-35 percent of the market in the mid- and northern regions of the country. The highest penetration has occurred in the northwest where penetration now stands near 66 percent. However, the e-glass technology that has penetrated these regions is best at letting in visible light and retaining heat – making it most suitable in such climates. Windows coating technologies were not good at letting in visible light while reflecting infrared in southern climates. Windows that were good at screening the infrared required too much tint and did not meet consumer aesthetics. Because of this, e-Window technology has only penetrated the southern regions to two percent. The predominant window in the southern regions is installed with clear, single-pane glass.

The new CVD process allows the lead manufacturer to produce an e-Window that meets consumer aesthetics while screening out heat-producing infrared rays.

7.1 Analysis Assumptions and Data

The benefits analysis:

- Assumes the windows market consists of the top 50 home construction markets in the Southern climate zone for windows.
- The markets include Atlanta (Georgia); Phoenix and Tucson (Arizona); Riverside, San Diego, Los Angeles, and Orange County (California); Dallas, Houston, Austin, San Antonio, and Ft. Worth (Texas); and Orlando, Tampa, Ft. Lauderdale, Jacksonville, W. Palm Beach, Miami, and Sarasota (Florida).
- In 2000, 277,000 single-family homes were constructed in these markets.
- The average annual growth rate in single-family new home construction is 3.86 percent.
- Only new home construction is estimated.
- Current market penetration of low-e windows is 2 percent and ultimate penetration in new construction will maximize at 80 percent, taking 20 years to achieve.
- The weighted average electricity savings in new single-family homes constructed in these markets is 910 kWh of cooling load. The weighted average electricity consumption in these homes for both heating and cooling equals 6,000 kWh.
- That without the DOE Industrial Materials for the Future R&D, development by industry of these e-Windows would have taken an additional five years to achieve.

Data for these assumptions came from:

1. *Housing Facts, Figures and Trends*, National Association of Home Builders, June 2001.
2. Windows Fact Sheets, Efficient Windows Collaborative.

Based on these data and assumptions, we estimate a cumulative energy savings from 2001 to 2030 of 16.7 trillion Btu. Figure 12 shows the annual and cumulative energy savings year-by-year for this period.
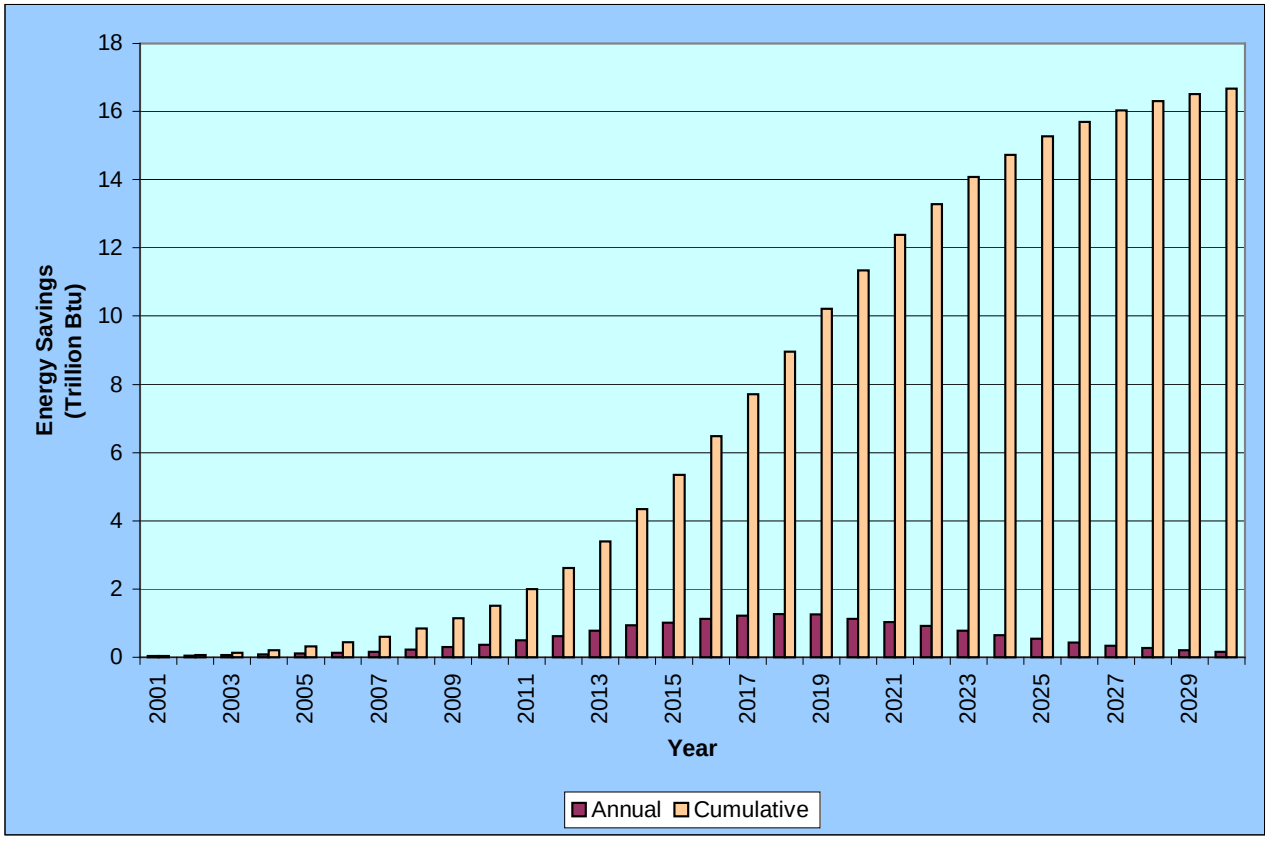
Figure 12: Annual and Cumulative Energy Savings from Use of Pyrolytic Glass in Southern Regions of the United States: 2001-2030