On-line Deposition of Oxides on Flat Glass

by Mark D. Allendorf

Oxide-coated glass is a major industrial product, with more than 110 million ft^2/year of flat glass coated by chemical vapor deposition (CVD). Fluorine-doped tin oxide for use as low-emissivity or solar-control architectural glass is the largest product; but a wide range of other coatings are produced as well, including the oxides of silicon, titanium, aluminum, zinc, cobalt, iron, and chromium. Products incorporating coated glass include (in addition to architectural glass) flat-panel displays, mirrors, anti-static glass, abrasion-resistant coatings on glass containers, and sodium diffusion barriers. These materials and their deposition chemistries have been recently reviewed.[1]

Although on-line CVD methods are currently the most economical way to deposit films on flat glass, most coated glass is still produced by batch sputtering methods. Only about 20% of all coated flat-glass is coated by CVD. This is partially because sputtering techniques were developed first, but also because developing a successful on-line CVD process is difficult. A recent workshop, sponsored by the U.S. Department of Energy's Office of Industrial Technologies and PPG Industries, and held in conjunction with the Glass Manufacturing Industry Council, highlighted industry goals for further development of coating technologies, technical hurdles, and the research needed to surmount the hurdles. A copy of this report is available on the Web.[2]

In this article, we describe some of the challenges in optimizing on-line CVD-coating technologies and developing new processes, using examples from our work and that of others. In particular, we focus on the gas-phase chemistry because it is rate limiting for tin oxide, the material most commonly deposited by on-line CVD (this may also be true for other chemistries; see below). We discuss experimental and theoretical techniques that can be used to develop gas-phase mechanisms and briefly review some of the relevant work. Such mechanisms are a key element in process models, which are becoming essential to rapid scale up of industrial processes. Lack of reliable thermodynamic and kinetic data is becoming an increasingly critical problem, however, and theoretical methods may be the only way to fill the gap in the short term.

Requirements for On-line Coating

The technology required to successfully apply CVD methods to on-line coating of glass has been recently reviewed by McCurdy.[3] First, coatings must be thickness insensitive, so that variations in layer thickness are not visible to the eye. This represents a major challenge, because the relatively large activation barriers for deposition accentuate temperature-induced nonuniformities. For example, activation barriers for tin oxide formation by CVD from tetramethyl tin ($Sn(CH_3)_4$) and oxygen are typically between 25 and 42 kcal/mol. Furthermore, the glass ribbon moving on a float-glass manufacturing line (Fig. 1) can be as wide as 4 m, requiring precise and uniform control of precursor delivery. Second, deposition chemistry must be very fast to accommodate line speeds greater than 25 cm/s; typically, only 1–2 s are available to complete the deposition process. Not only does this severely limit the range of chemistries available, it raises a host of other problems, including reaction of premixed reactants before deposition and gas-phase nucleation of particles. The final requirement is for flexible deposition technologies. This includes features such as chemically stable precursors that can be delivered in high concentrations (liquid precursors are usually necessary), reactor designs that enable uniform delivery over the entire width of the glass ribbon, and deposition equipment that can be quickly converted from one product to another.

A fourth factor to consider is the formation of coating defects, either during deposition, or later during annealing. Defects include homogeneous particle formation and chlorine-induced pitting. Particles are normally not a problem, since particles formed in the gas phase are typically small (maximum diameters in the range of a few hundred nm) and

Fig. 1. Interior view of a float tank in which flat glass is formed. The picture shows molten glass spreading on the surface of the molten tin. The two wheels attached to rods cause the glass to move along the surface and assist in spreading it to its full width. Coatings deposited by CVD are applied downstream after the glass reaches a temperature of 600 – 700°C. (Source: D. A. Strickler, Pilkington Libbey-Owens-Ford Co.)

thermophoresis drives them away from the hot deposition surface. However, extensive buildup of particles due to prereaction in the delivery lines or condensation of reaction byproducts in the exhaust lines can severely reduce process run times. Decomposition of chlorine-containing precursors leads to gas-phase species such as HCl that can react with sodium in the glass to form NaCl nuclei that either vaporize in the annealing lehr or hydrolyze when exposed to air. The resulting fine pits (see Pantano *et al.*)[4] appear to the eye as haze (Fig. 2).

Meeting these requirements requires a great deal of technical expertise, including knowledge of chemical reactions, fluid dynamics, heat and mass transfer, and materials science. It is thus easy to see why many years of development are often required to implement a new deposition technology. Lack of fundamental knowledge in many of these areas inhibits accelerated development of on-line CVD processes for new materials, such as those required for on-line formation of electrochromic materials. Perhaps the most immediate need is for new precursors whose deposition kinetics can meet the requirements of float-line deposition. Gordon recently reviewed progress in this area,[1] demonstrating that a broad range of new compounds are available with properties that make them attractive potential candidates for oxide CVD precursors. These properties include reasonable vapor pressures, low melting points (*i.e.*, liquids at room temperature), and ease of handling (*e.g.*, lack of sensitivity to air and water vapor, low toxicity). Little work has been done to evaluate deposition rates, however. This points to the need for rapid screening methods to determine deposition rates over a wide range of processing conditions.

Once a given precursor is selected, however, it is important to understand its reactivity, in the gas phase as well as on the surface. In some of the most important CVD processes used in the glass industry, gas-phase reactions are rate controlling. This is due to the fact that relatively low temperatures are used, leading to partial cracking of the initial reactant followed by radical chain reactions that accelerate further decomposition. For example, in the case of tin oxide CVD from dimethyltindichloride (DMTC),[5] the loss of the first methyl radical is apparently rate limiting:

$$(CH_3)_2SnCl_2 \rightarrow CH_3SnCl_2 + CH_3 \quad (1)$$

As a result, complex mechanisms involving dozens of species and hundreds of reactions are needed to fully model the chemistry. Both thermodynamic data (heats of formation, entropies, and heat capacities) and rates of many elementary reactions are needed. In the remainder of this article, we briefly review the state of knowledge in the areas most important to on-line coating and point to areas where more work is necessary.

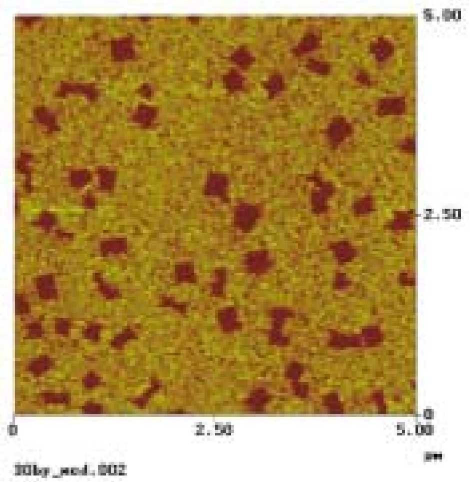

FIG. 2. Morphology of a commercial tin-oxide coating on a glass container revealed by atomic-force microscopy. Square holes in the coating are caused by NaCl formation, resulting from the reaction of chlorinated reactants with sodium in the glass. (Source: C. Pantano, Penn State University.)[4]

Quantum-Chemistry Approaches to the Prediction of Molecular Thermochemistry

While the extensive efforts devoted to hydrocarbon chemistry have resulted in accurate thermodynamic data for most species relevant to hydrocarbon oxidation, comparable data are almost entirely lacking for most CVD precursor compounds and their metal-containing decomposition products. It is thus very difficult to develop chemical mechanisms that can be coupled to process models. Fortunately, the quantum-chemistry methods that have been extensively developed over the last two decades are now capable of predicting thermodynamic properties for many main-group compounds with accuracies of ± 2-3 kcal/mol.[6,7] Data for transition-metal com-

Table I. Comparison of heats of formation (kcal mol^{-1}) predicted by the BAC method with literature values. Literature values are from Gurvich ***et al***.[20] unless otherwise noted. Units are kJ mol^{-1}.

	ΔH°_{298} (Calc)	ΔH°_{298} (Obs)		ΔH°_{298} (Calc)	ΔH°_{298} (Obs)
$BHCl_2$	-60.6 ± 4.3	-60.0 ± 1	SiH_2Cl_2	-74.4 ± 4.6	-76.6 ± 13[a]
BH_2Cl	-20.3 ± 4.3	-19.3 ± 4.8	$SiCl_2$	-36.2 ± 15.6	-39.0 ± 2.4
C_2H_2	-20.8 ± 4.3	-20.1 ± 0.1	SiH_2	64.8 ± 9.2	65.4 ± 1.2
C_2H_2	12.3 ± 4.3	-12.5 ± 0.1	$SiHF_2$	-288.6 ± 5.6	-291.8 ± 5.0[a]
CH_2	34.9 ± 6.3	34.9 ± 0.1	$Si(OC_2H_5)_4$	-317.4	-314.3 ± 1[c]
C_2H_2	28.8 ± 6.7	25.6 ± 1.4	SiO	-26.7±16	-26.4 ± 2.0[a]
NH	87.0 ± 4.6	90.1 ± 4[a]	$AlCl_3$[b]	-141.5[b]	-139.8 ± 0.7
NH_2	46.1 ± 4.6	45.4 ± 2[a]			

[a] *JANAF Thermochemical Tables* (Ref. 21). [b] *BAC-G2 method; see Ref. 22.* [c] *R. Walsh in* The Chemistry of Organic Silicon Compounds, *S. Patai and Z. Rappoport, Editors, p. 371, Wiley, New York (1989).*

pounds are still problematic, because much less work has been done for them than for main-group compounds. Some examples of predicted heats of formation for main-group compounds from our own work using the Bond Additivity Corrected (BAC) method are shown in Table I. This method provides accurate heats of formation for compounds in the first through third rows of the main-group periodic elements (H – Kr).[8]

Even higher accuracies may be achievable using composite methods such as G2 and CBS,[7] which combine multiple calculations at lower levels of theory to achieve results equivalent to higher-order (but more computationally intensive) levels. Such methods have not been extensively tested for the larger compounds typically of interest in CVD and thus may contain uncharacterized systematic errors. In particular, we have found surprising inaccuracies in the G2 predictions for main-group compounds containing fluorine, oxygen, or chlorine ligands. For example, the heat of formation (0 K) for GaF_3 predicted by G2 is –111.5 kcal/mol, while the accepted literature value is –219.5 ± 6.5 kcal/mol.[9] Similarly, G2 predicts –158.1 kcal/mol for the (0 K) heat of formation of $SiCl_3$, while the accepted value is –76.0 kcal/mol.[10] The source of the error in the GaF_3 calculation has been determined and can be remedied.[9] In the case of $SiCl_3$, however, we have not traced the source of the anomaly, although it appears to involve one of the calculations at a level above the second-order Møller-Plesset perturbation theory. These results indicate that even after the extensive efforts of recent years, the results of *ab initio* calculations must be viewed with caution when these methods are applied to new chemistries. Confidence can be obtained by examining trends predicted for compounds in a homologous series (*e.g.*, the heats of formation for $SiCl_nH_{4-n}$ should vary linearly), performing higher-level calculations for comparison with lower-level results, and/or using experimental data for calibration. Unfortunately, the experimental data are sorely lacking for most compounds of interest in CVD, particularly for organometallic compounds. Expanded research to establish accurate experimental values for molecular heats of formation would be a valuable contribution to both CVD modeling and quantum chemistry.

Gas-Phase Kinetics

Again, in contrast to hydrocarbon chemistry, experimental measurements of reaction rates relevant to coatings on glass are largely absent from the literature (silane oxidation being one notable exception). The high-temperature chemistry can be exceptionally complex; for example, Fig. 3 illustrates some of the reaction pathways and energetics available in the oxidation of silane, which is used to deposit silica in multilayer or graded-index coatings. The most extensively treated CVD chemistry relevant to coatings on glass outside silane oxidation is the oxidation of organotin compounds studied by Gordon and coworkers. In their work on DMTC,[5] they employed a gas-phase mechanism that included 120 reactions. Only 20 of these reactions actually involved tin-containing species, and of these, all but four had to be estimated.

Experimental measurements of precursor decomposition and reaction kinetics are available for a limited number of precursors. Aside from silane oxidation, which is not fully understood in spite of a large number of investigations (see for example Reference 11 and references therein), decomposition and/or oxidation of precursors for tin oxide;[5] fluorocarbon oxidation (relevant to fluorine doping of tin oxide);[12] titanium dioxide ($TiCl_4$;[13] titanium isopropoxide);[14] silica (tetraethoxysilane (TEOS);[15] $SiCl_4$[16]), indium oxide,[17] and zinc oxide (dimethyl zinc)[18] have been examined. The extent of these investigations is limited in most cases, and even in those instances where multiple investigations were performed, significant questions remain, as is shown by the following example for indium oxide precursor chemistry.

Indium tin oxide (ITO) films have higher reflectivity in the near IR than fluorine-doped tin oxide while maintaining high transmission in the visible, providing coatings that can be used for control of solar heat flux in warm climates. Gas-phase chemical kinetics are expected to play a role in the deposition, since organoindium compounds have relatively weak bonds and are also Lewis acids that can react with electron donors such as water vapor. Trimethyl indium (TMI) provides a good starting point for understanding the decomposition of indium-containing organometallic precursors, because it is easily volatilized. Several investigations of the high-temperature chemistry of TMI are reported in the literature (see Ref. 17 and references therein). Most assign the observed removal rate of TMI to gas-phase reactions, estimating that the In-CH_3 bond energy is between 35 and 54 kcal mol^{-1}.

Our recent flow-reactor experiments using a molecular-beam mass spectrometer to detect reactants and products show, however, that this chemistry is dominated by surface reactions.[17] Selected results are shown in Fig. 4. The investigation demonstrates that autocat-

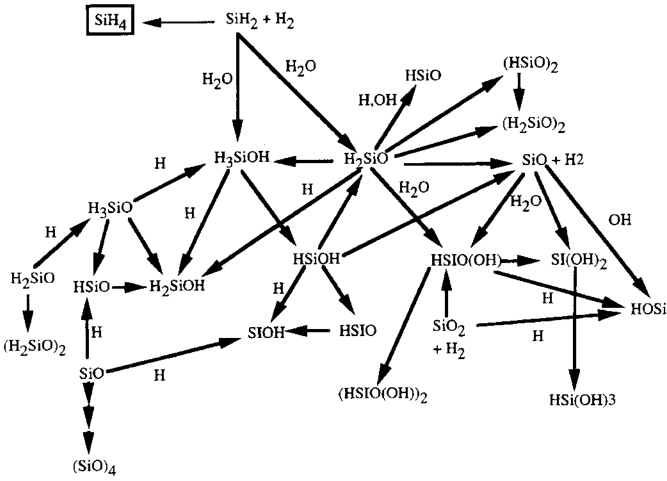

FIG. 3. Schematic of silane oxidation paths, determined by ab initio calculations. The direction of the arrow indicates the exothermic direction of the reaction (adapted from Ref. 11).

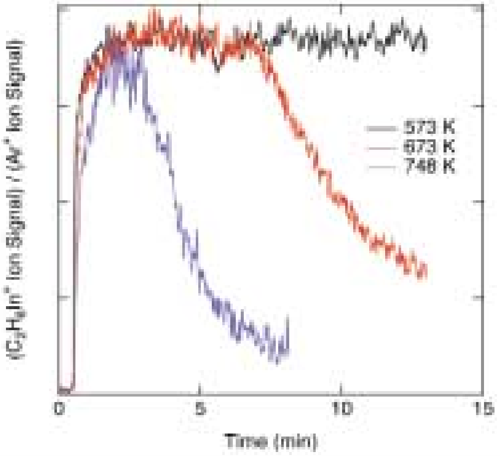

FIG. 4. Time-dependent decomposition of trimethylindium in a flow reactor, as determined by mass spectrometry (Ref. 17). Note that decomposition is preceded by a short induction period, followed by a time-independent decomposition rate. The results indicate that an autocatalytic process on the reactor walls is occurring.

alytic heterogeneous processes dominate TMI decomposition in flow tubes. As a result, the In-CH_3 bond energy derived from such measurements is significantly in error, based on comparisons with high-level theoretical predictions (Fig. 5). Thus, although flow-tube experiments have been widely used to measure CVD precursor decomposition rates because they can be effective and relatively simple, experiments must be performed to evaluate the extent of surface reactions (*e.g.*, surface/volume ratios must be varied to isolate the heterogeneous component). Data from shock tubes, very-low-pressure pyrolysis, or laser flash photolysis experiments may be preferable, because these techniques can be essentially wall-less, thus eliminating the complications of heterogeneous reactions.

Theoretical Approaches to CVD Reaction Modeling

Given the scarcity of experimental kinetic data for most CVD chemistries, use of theoretical methods is essential for the development of CVD mechanisms. Multiple theoretical techniques are usually required, beginning with *ab initio* methods to calculate thermochemistry, as described above. With heats of formation in hand for the species of interest, reaction enthalpies can be calculated, allowing one to identify likely reaction pathways. At this point, equilibrium calculations become useful, since they can be used to identify stable products as a function of deposition conditions. The value of equilibrium predictions is limited, however, because CVD systems usually do not reach temperatures high enough for the gas phase to reach complete equilibrium. Thermal decomposition of $TiCl_4$, a common precursor to titanium dioxide, in hydrogen carrier gas provides an example of this. Kinetic studies indicate that time scales on the order of several seconds are needed to reach equilibrium at 1000 K and 1 atm pressure. Thus, thermochemistry is only a point of departure in the development of a kinetic mechanism.

Two basic theoretical methods are needed to predict rate constants for elementary reactions. Reactions without an activation barrier (loose transition states; see Fig. 6), such as the initial step in $TiCl_4$ decomposition ($TiCl_4 \rightarrow TiCl_3 + Cl$),[13] require variational transition-state theory, usually RRKM/master-equation methods because there is no well-defined transition state. Reactions with an activation barrier (tight transition states; Fig. 7) such as the initial step in silane pyrolysis ($SiH_4 \rightarrow SiH_2 + H_2$), are, in principle, much more straightforward to treat because the location of the transition state (at the top of the activation barrier) is clear. The geometry and thermochemistry of the transition state can be determined using *ab initio* methods, although this is not nearly as straightforward as predicting thermochemistry for stable species. Again, silane oxidation has been thoroughly treated in this instance. For example, Zachariah and Tsang have combined RRKM and BAC-MP4 calculations to assemble a detailed kinetic model of this chemistry (Fig. 3).[11] Methods for performing RRKM calculations to determine temperature- and pressure-dependent rate constants are discussed in recent textbooks (see for example Ref. 19).

Conclusions

CVD of optical coatings using online manufacturing methods is now a large-scale commercial enterprise. Because this is a continuous process, online CVD can be an economical way to produce highly value-added products from float glass. However, there is a strong need for new science concerning the high-temperature chemistry of these processes. In particular, accurate data concerning gas-phase chemical thermodynamics and kinetics are of importance. Expanded experimental and theoretical efforts using the techniques just described will undoubtedly contribute to accelerated development and scale-up of new on-line CVD processes. ■

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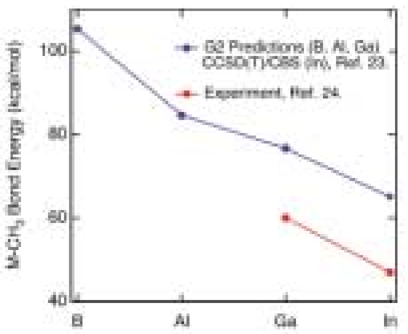

FIG. 5. $(CH_3)_2M—CH_3$ bond energies predicted by G2 (M = B—Ga or coupled-cluster (M = In) calculations. Data from Ref. 23. Data of Jacko and Price are found in Ref. 24.

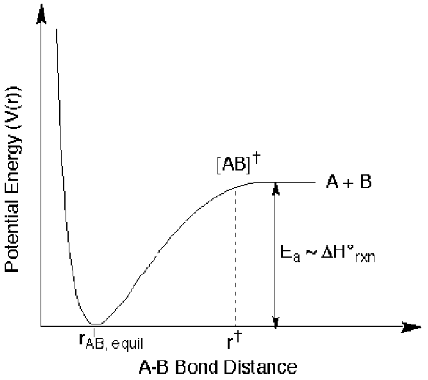

FIG. 6. Schematic of the potential-energy curve for a reaction with a so-called loose transition state, in which there is no activation barrier (other than the endothermicity of the reaction).

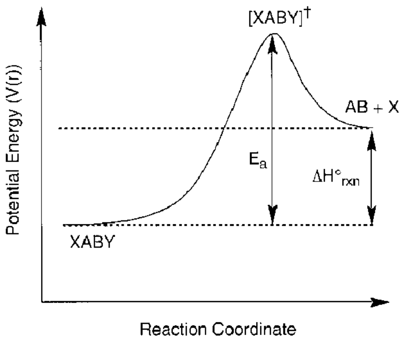

FIG. 7. Schematic of the potential-energy curve for a reaction with a tight transition state, in which the location of the transition state along the reaction coordinate (the x axis) is at the top of the activation barrier.

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