Thermodynamics and Reaction Pathways in the Decomposition, Oxidation, and Hydrolysis of Monobutyltintrichloride

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Fluorine doped tin oxide (FTO) is a transparent conducting oxide that is widely used as a coating on glass. Low-emissivity windows are the largest product, but FTO coated glass for photocopier applications, refrigerators, solar cells, computer screens, and automotive windshields is also produced. On-line deposition of tin oxide coatings using chemical vapor deposition methods has proved to be an economical and effective method; such coatings adhere very strongly to the glass and are thus more durable than sputtered coatings and can be bent for applications such as windshields. Optimization of such processes is extremely difficult, however. Due to the speed of the moving glass ribbon (roughly 30 cm/s), the time available to deposit a coating with the necessary thickness (of order 100-1000 nm) is only 1-3 sec. Coatings must be highly uniform, particularly for architectural applications; thickness nonuniformities as small as a few tens of angstroms can be visible to the eye. Reactant conversion efficiencies can also be poor, leading to higher production costs and the need to dispose of the waste.

Chemical reactions among the reactants are likely to occur in the heated gas boundary layer above the glass. In some cases, these are found to be rate limiting.[1] It is thus important from a process modeling viewpoint to understand the extent of these reactions. Accurate thermodynamic data are an essential part of this understanding, since these data can be used to calculate bond energies, equilibrium concentrations, and are necessary for predicting reaction rates.

In this paper, *ab initio* quantum-chemistry methods are used to predict heats of formation and other thermodynamic properties for gas-phase tin compounds relevant to the chemical vapor deposition of tin oxide coatings from monobutyltintrichloride (MBTC). For most compounds, we use the BAC-MP4 method (see for example Ref. 2) The results are used to predict equilibrium concentrations and identify important reaction intermediates. Bond energies and reaction enthalpies are also examined to suggest likely reaction pathways. The results suggest that, when water vapor is present, tin hydroxides such as $SnCl_3OH$ are the species that transport tin to the growth surface. These species form when the MBTC decomposition products $SnCl_3$ and $SnCl_2$ react with water vapor, initially forming the complexes Cl_3SnOH_2 and Cl_2SnOH_2. Direct reaction between $SnCl_2$ or $SnCl_3$ and oxygen can occur, leading to formation of peroxide species such as Cl_3SnOO. However, these species are either not thermodynamically stable at reaction temperatures or lack effective reaction pathways that lead to stable hydroxide products. Thus, the calculations suggest that deposition precursors formed in the gas phase do so via reaction of MBTC decomposition products with water, rather than with molecular oxygen.

Independent of thermodynamic considerations, experimental evidence shows that tin oxide cannot be deposited in the absence of oxygen; mixtures of water vapor and MBTC lead to carbon formation in CSTR experiments.[3] Conversely, tin oxide can be deposited from mixtures of MBTC and oxygen, but the deposition rate is much slower than when water vapor is included with the oxygen. Experiments we performed in a high-temperature flow reactor also indicate that MBTC reacts rapidly with a clean silica reaction tube in the absence of oxygen, but quickly forms carbon on the tube walls. This carbon can be removed by reaction with oxygen at 773 K to form CO_2.[3] Thus, the role of oxygen in the tin oxide CVD system may be to maintain a carbon-free surface, rather than to oxidize the tin precursor, while water vapor reacts quickly with the immediate decomposition products of MBTC to form tin hydroxides that react with the surface to form tin oxide.

ACKNOWLEDGEMENTS

This work is supported by the U.S. Dept. of Energy Office of Industrial Technologies Glass Industry of the Future team and by PPG Industries, Inc., Pittsburgh, PA.

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