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Chemical vapor deposition of tin oxide: Fundamentals and applications

A.M.B. van Mol [a,*], Y. Chae [b], A.H. McDaniel [b], M.D. Allendorf [b]

[a] *TNO Science and Industry, Eindhoven, The Netherlands*
[b] *Sandia National Laboratories, Combustion Research Facility, Livermore, CA, USA*

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Abstract

Tin oxide thin layers have very beneficial properties such as a high transparency for visible light and electrical conductivity making these coatings suitable for a wide variety of applications, such as solar cells, and low-emissivity coatings for architectural glass windows. Each application requires different properties of the tin oxide layer. These properties can be tuned by adjusting the parameters of the chemical vapor deposition (CVD) process, the main technique used for applying the tin oxide layer to the substrate. This paper discusses the state of the art of the kinetic models for tin oxide CVD. In the case of organometallic precursors the gas-phase chemistry may be initiated by cleavage of the tin–carbon bond, followed by radical-driven chain reactions that enhance the overall decomposition rate. However, in commercial tin oxide CVD reactors the gas-phase temperature may be too low or the residence time too short for these reactions to occur, thereby favoring surface chemistry. Preliminary investigations of the MBTC–H_2O–O_2 chemistry indicate that a mechanism comprising the reaction between gaseous oxygen and an adsorbed MBTC–H_2O complex is a plausible model.

Keywords: Tin oxide; CVD; Solar cell; Low-E windows

1. Introduction

Thin films of transparent conductive oxides (TCO) find use in a wide variety of technologies. In particular, thin films of fluorine-doped tin oxide (SnO_2:F) deposited by atmospheric pressure chemical vapor deposition (APCVD) are desirable due to a number of useful properties, including high transparency for visible light, low electrical resistivity, high reflectivity for infrared light, high mechanical hardness, and good environmental stability.

In a conventional CVD process gaseous precursors are transported to a reactor chamber, where under influence of a heated substrate they react, resulting in a solid film on the substrate. The reactions can take place both in the gas-phase above the substrate and on the surface of the substrate. The type of precursors and the reactions that take place determine the final properties of the layer.

Both inorganic and metalorganic precursors in conjunction with O_2 and/or H_2O provide fast enough deposition rates for the process to be commercially viable and are thus often used to deposit tin oxide in industrial processes. This is particularly important when tin oxide is deposited on flat glass, since this is a continuous process in which the deposition time is limited by the speed of the glass moving on the line [1]. Typically, only 1–3 s are available for depositing a coating ranging in thickness from 1000–7000 Å. Although it is possible to deposit tin oxide from many different organometallic precursors [2], the ones most commonly used industrially are tin tetrachloride ($SnCl_4$, TTC), dimethyltindichloride ($(CH_3)_2SnCl_2$, DMTC) [3–7] and monobutyltintrichloride (n-$C_4H_9SnCl_3$, MBTC) [8,9].

Tin oxide thin films are used in products like energy-conserving (low emissivity; low-E) windows, solar cells, smart windows, flat-panel displays (FPD), heated windows, etc. A different set of properties is required for each type of application. For example, very flat layers are required for low-E windows, while hazy layers are needed for solar cells. A thorough understanding of the chemical process would therefore be a tremendous aid in optimizing the layer properties for each of the applications.

* Corresponding author.
E-mail address: ton.vanmol@tno.nl (A.M.B. van Mol).

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CVD is a complex process, involving both gas-phase and surface chemistry, as well as the hydrodynamics of the reactor system. The design of CVD processes in industry is therefore rarely based on a scientific approach, but rather on empirical results and experience. As a result, optimal conditions do not always result. For example, low process yields and high product rejection rates (usually due to optical nonuniformities) are common. The lack of more fundamental understanding of the coating process was identified as one of the major problems in this industry at a recent roadmapping exercise for the development of coatings glass industry [10].

The need for substantial improvements in coating manufacturing processes is illustrated by two examples [10]:

- In the deposition of coatings, such as tin oxide on flat glass, a best-case yield of around 70% is achieved using CVD, but this can be as low as 50%. If a coating is not applied, the yield is typically 75%–80%. This means that coating methods substantially reduce the overall productivity of the glass manufacturing process, resulting in large amounts of rejected glass that must be ground and remelted. Such high rejection rates represent an enormous cost in energy. On average, roughly 4×10^{10} kJ/year, must be expended to remelt this glass.
- The efficiency of reactant utilization in CVD on float glass can be as low as 10%, necessitating the installation of expensive chemical scrubbing units or incinerators and requiring landfill of more than one million kg/year of waste.

Because of the high cost of experimentally determining the effects of process variables on deposition rates, detailed process models are seen as the only economical method of making significant improvements in existing industrial deposition methods. Fundamental knowledge concerning the deposition chemistry is necessary to develop process models that can effectively simulate the CVD process across a broad range of potential process variables.

In the remainder of this article, we discuss the requirements of tin oxide coatings in various applications, such as solar cells and low-E windows, and how they can be affected by processing conditions. We then summarize recent efforts to develop detailed chemical models describing the tin oxide CVD process, which have lead to greatly improved ability to predict growth rates as a function of reactor conditions.

2. Applications

2.1. Architectural glazing

Glass coated with fluorine-doped tin oxide is an excellent energy-conserving window. Tin oxide has a plasma wavelength of about 2000 nm. The free electrons reflect the infrared (IR) radiation for wavelengths longer than the plasma wavelength, so heat stays inside the building. For an optimal performance, the IR reflectivity and the specular transmission for visible light of the tin oxide layer should be as high as possible. Both are determined by an optimum in layer thickness, carrier concentration and mobility. Also, the requirement of high specular transmission means that the layer should have a very low surface roughness, i.e. the grain size has to be small.

Additionally, due to the high volume production and the low added value, the production process must be inexpensive and fast, and preferably be integrated in the glass float line. These requirements make tin oxide APCVD naturally a very good candidate.

2.2. Thin-film solar cells

Thin-film solar cells are becoming an attractive means for the production of electrical energy. The TCO used as a front contact is an essential part of the cell. In the case of a glass superstrate cell, APCVD-grown tin oxide is the preferred TCO because of the combination of its processing convenience and good layer properties.

These layers of course need a high optical transmittance, necessary for efficient transport of the light into the active stack, and good electrical conductivity, required to obtain a low transport loss of the generated electrical energy. These two properties are inversely linked to each other through the carrier concentration. High doping levels increase the electrical conductivity, but also decrease the optical transparency in the visible and near infrared region due to free carrier absorption and reflection. The optimum level depends on the quantum efficiency spectrum of the active layer, which is, for example different for a-Si:H and μc-Si:H cells.

A key technology to increase cell efficiency in thin-film solar cells is optimization of the light trapping effect. This effect, visualized in Fig. 1, results in a longer path length of the light through the active material.

One of the most important methods to obtain effective light trapping is tuning of the surface morphology, where both the surface roughness and the shape of the surface features are important parameters to be optimized.

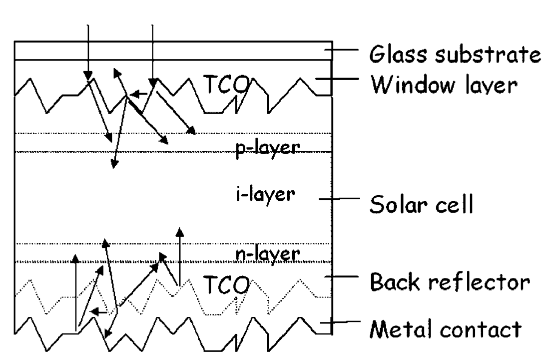

Fig. 1. Cross-section of an a-Si:H solar cell. The TCO electrode at the front window exhibits a rough surface causing light trapping.