TIN OXIDE DEPOSITION IN A COLD-WALL CVD REACTOR: COMPUTATIONS AND EXPERIMENTS

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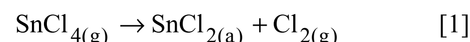
Chemical Vapor Deposition (CVD) processes focus on the formation of thin films on heated substrates from chemically reactive gases. These solid films are used in various industrial applications for producing gas sensors, semiconductors, transducers, insulators and other opto-electronic devices. Tin oxide (SnO_2) thin films have attracted great attention in the last decades due to the stability of their electrical, optical, chemical and mechanical properties. In particular, they remain stable up to high temperatures and they have excellent resistance at room temperatures as well as good adhesion to many substrates. Their properties depend strongly on the deposition technique and the post deposition treatment. Various methods including spray pyrolysis, vacuum evaporation, RF sputtering, chemical vapor deposition and plasma-enhanced CVD have been used for the preparation of tin oxide films. Tin chlorides and metal-organic compounds have been used in many studies as source materials for tin (1, 2, 3, 4). Most of these studies have focused on the optical and electrical properties as well as the surface morphologies of the produced films. However, limited attention is given to the chemical mechanisms involved in the gas phase and on surfaces during the growth of tin oxide layer (1, 3).

Recently, the properties as well as the structure and surface morphology of SnO_2 films from tin tetrachloride ($SnCl_4$) by employing the CVD process have been reported (5). In the present work we decided to further study the deposition of tin oxide films so that a better knowledge of the CVD process be obtained. Clearly, any attempt to design tin oxide deposition with reasonable constraints on thickness uniformity requires a remarkable number of experiments. This certainly would be costly and probably inefficient. In this aspect, the main goal of this study is to identify the physical and chemical phenomena involved in tin oxide deposition, to determine its growth kinetics, and finally, to develop a mathematical model able to simulate the overall reactor performance. Of particular interest, is to examine the possibility of coupling a detailed three-dimensional computational fluid dynamics (CFD) model with a relatively simple chemical kinetic scheme for performing efficient design and optimization of the CVD process.

This design methodology is implemented in a homemade horizontal cold-wall reactor where tin oxide deposition is experimentally studied on silicon substrates at atmospheric pressure conditions. The influence of the two most important parameters, gas inlet composition and substrate temperature on the deposition rate, has been experimentally investigated. A set of measured deposition rates in well-defined operating conditions has been used to determine the growth kinetics of tin oxide films.

The complexity of the surface and bulk chemical reactions involved in SnO_2 deposition is represented by a Langmuir-Hinshelwood type kinetic mechanism, which consists of the two following steps:



$$SnCl_{4(g)} \rightarrow SnCl_{2(a)} + Cl_{2(g)} \qquad [1]$$

$$SnCl_{2(a)} + O_{2(g)} \rightarrow SnO_{2(s)} + Cl_{2(g)} \qquad [2]$$

At equilibrium, the SnO_2 deposition rate is given by the equation:

$$R_d = \frac{K_a C^s_{SnCl_4} K_d C^s_{O_2}}{K_a C^s_{SnCl_4} + K_d C^s_{O_2}} \qquad [3]$$

The values of the kinetic coefficients K_a and K_d, at different process temperatures, were determined by a trial and error procedure so that a good agreement between theoretical predictions and experimental measurements is obtained. The CFD model used for the simulations involves the conservation equations of mass, momentum, and energy under steady states conditions (6). The set of coupled nonlinear partial differential equations are discretized by the finite-volume method and solved on a 3D multi-domain grid (7).

The Langmuir-Hinshelwood type kinetic model coupled with the CFD code was then used for a thorough analysis of the effects of important physical and operational factors on the overall reactor performance. Simulation results have indicated that key parameters that could be varied independently and influence substantially the deposition rate are the substrate temperature, the gas inlet composition and the total feed rate. The results are suggestive of modifications in the operating parameters that could enhance the uniformity of the tin oxide layer thickness.

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REFERENCES

1. R.N. Ghoshtagore, J. Electrochem. Soc., **125**, 110 (1978).
2. D. Davazoglou, Thin Solid Films, **302**, 204 (1997).
3. M.B Amjoud, F. Maury, S. Soukane, P. Duverneuil, Surface and Coatings, **100-101**, 169 (1998).
4. S. Tamura, T. Ishida, H. Magara, et al, Appl. Surf. Sci., **169-170**, 425 (2001).
5. A. Koutsogianni, D. Tsamakis, J. Physique IV, **11Pr3**, 377 (2001).
6. C. Kleijn, C. Hoogendoorn, Chem. Eng. Sci., **46**, 321 (1991).
7. T.C. Xenidou, M.K. Koukou, A.G. Boudouvis and N.C. Markatos, J. Physique IV, **11Pr3**, 183 (2001).