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Chemical Vapor Deposition of Refractory Metals and Ceramics

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MRS

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Chemical Vapor Deposition of Refractory Metals and Ceramics

Symposium held November 29-December 1, 1989, Boston, Massachusetts, U.S.A.

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Preface

The papers contained in this volume were originally presented at the Symposium on the Chemical Vapor Deposition of Refractory Metals and Ceramics held at the Fall Meeting of the Materials Research Society in Boston, Massachusetts on November 29 - December 1, 1989. This symposium was sponsored by the Directorate of Electronic and Materials Sciences - Air Force Office of Scientific Research and the Army Research Office. The object of the symposium was to promote dialogue between scientists and engineers who are working in the field of chemical vapor deposition of refractory materials. With this focus the symposium was able to directly address issues which are often bypassed in other vapor deposition meetings that principally concentrate on low-temperature process for electronic materials.

The sessions in the symposium were designed to move smoothly from fundamentals/modeling and diagnostics, emphasizing the understanding and monitoring of basic deposition processes, through process-microstructure and microstructural-mechanical property relationships which deal with understanding and predicting deposit characteristics. Additional sessions dealt with novel/large-scale technologies allowing some very innovative ideas to be presented, and metal-organic chemical vapor deposition, which is a blossoming area resulting in lower deposition temperatures and heretofore impossible to produce coatings.

The invited papers, presented by leaders in the field, laid the groundwork for the various sessions of the symposium. The invited papers on fundamentals/modeling clearly demonstrated the high degree of sophistication that has just recently been obtained in understanding and modeling chemical vapor deposition, and highlighted the long way we still have to go. The invited papers on process-property relationships displayed the breadth of our understanding, which is just beginning to depart from the empirical. The invited paper on metal-organic chemical vapor deposition clearly demonstrated the enormous versatility of the technique, as well as its certain pitfalls.

January 19, 1990

T.M. Besmann
B.M. Gallois

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PART I

Fundamentals/Modeling

BENEFITS AND LIMITS OF THE THERMODYNAMIC APPROACH TO C.V.D. PROCESSES

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ABSTRACT

This paper intends to develop and illustrate by a few examples the principles of thermodynamic analysis which can be applied at an early stage to assist in selecting the following:

- the material to be deposited for a well-defined application,
- the nature of reactants,
- the range of experimental parameters.

Specific emphasis will be given to the main problems relating to data selection: assessments, availability of coherent data, sensitivity of results to data accuracy, etc.

Finally, the validity of a thermodynamic approach at equilibrium will be discussed with a view to optimizing a dynamic non-equilibrium process.

INTRODUCTION

The authors have been involved in a wide variety of studies in which a chemical vapour deposition process has first had to be defined and then optimized. In the light of these studies, their laboratory has tended to adopt a step-by-step approach which is considered to be the safest for ensuring successful investigation of any new problem [1]. This procedure can be divided basically into four stages:

- A-priori thermodynamic approach to assess the chances of success of the method: determination of reactant gases, phases likely to be formed from the initial gas phase but also by reaction with the substrate and with the furnace walls, thermodynamic simulation of the process, etc. A preliminary range of values will be obtained from this approach, and it will then be possible to choose the appropriate values for experimental parameters: temperature, flow meter fluxes, pump settings, etc. on the basis of this approach.
- Construction of a prototype reactor, based on the conclusions of the approach described above.
- Implementation of a series of experiments in order to evaluate the specific kinetic parameters of the reactions.
- Flux modelling and, if necessary, modification of the reactor to take into account the modelling results.

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This paper expands upon the first stage relating to thermodynamic optimization, with particular attention being paid to:

- stressing the importance of choosing the thermodynamic data,
- identifying possible sources of such data,
- using concrete examples to illustrate the various facets of this optimization.

IMPORTANCE OF CHOICE OF DATA

For many years, the present authors have made an a-priori thermodynamic approach to the complex chemical equilibria involved in the multi-phase systems prevailing in chemical vapour deposition reactors [2], [3], [4]. In particular, they have vigorously campaigned for the adoption of the global approach to a given chemical system, rather than a partial analysis based on considerations of the Gibbs' free energy of elementary reactions isolated from the general context. Even if, in the meantime, serious studies have been conducted on vapour phase transport and deposition processes [5-8] since the groundbreaking work of H. Schäfer [9], it is only over the past four to five years that the approach involving minimization of the global Gibbs' free energy of the system has been adopted by an increasing number of experimental workers.

There is every reason to be satisfied with this change in philosophy. However, new converts to the thermodynamic approach must be reminded of a crucial point: the importance of using high-quality data in the calculations. They should also be made aware of the repercussions that may arise through the use of data of doubtful accuracy or even false data. Before listing the possibilities of obtaining valid data in the world, two examples are given in order to stress the importance of choice and quality of thermodynamic data used.

The first example relates to silicon chlorides which are used intensively in the semi-conductor industry, especially for the selective deposition of epitaxial silicon from gaseous $SiCl_4$ - H_2 mixtures, on patterned silica-silicon wafers. It is assumed that the deposit selectivity results from the competition between silicon deposition and etching, caused notably by the simultaneity of the two following reactions [10]:

$$[SiCl_4] + 2[H_2] \rightarrow <Si> + 4[HCl]$$

$$[SiCl_4] + <Si> \rightarrow 2[SiCl_2]$$

It is thus of great importance to determine the location of the transition point between the two reactions. Graph A in figure (1) presents the experimental results [11]. Van der Putte et al. [12]. modelled the reactions involved. A thermodynamic calculation resulted in graph B which is shifted significantly towards low $SiCl_4$ partial pressures. They then adapted their model to take into account the transfer of material and obtained curve C. As the model still did not give a satisfactory account of the experimental results, they also included temperature gradient diffusion. This led to graph D which now comes close to the experimental values. In actual fact, there is a certain degree of dispersion in the available literature as regards thermodynamic data concerning gaseous molecules in the Si-H-Cl system [13] - [15]. Simply by using the experimental values with their extreme uncertainties, the silicon deposition rate curve shifts from position F to position E. [16] This simple observation shows that the use of sophisticated models to explain the difference between thermodynamic calculation and corresponding experiment is not necessarily the best solution and that, in some instances, it would be more advisable to determine the thermodynamic data more accurately: this is certainly the case for this system.

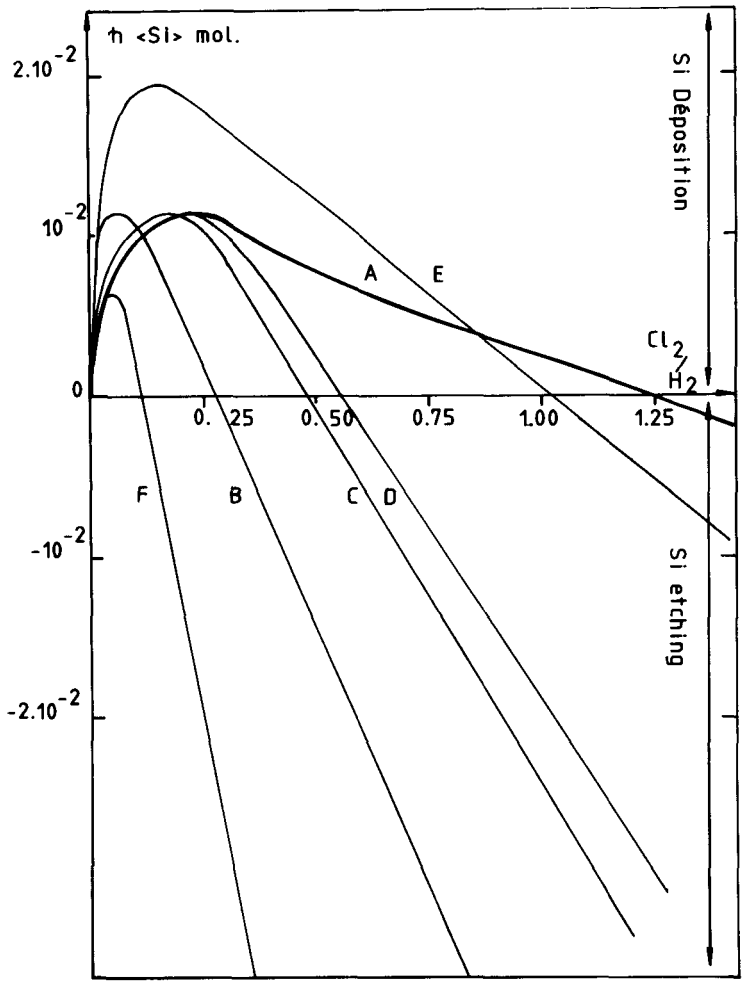

Fig.1 A-Experimental growth/etch curve as a function of the ratio Cl_2/H_2 in the input gas mixture $SiCl_4$-H_2 [11].
B-calculated growth/etch curve calculated using equilibrium model [12].
C-calculated growth/etch curve calculated using equilibrium model including diffusion [12].
D-calculated growth/etch curve calculated using equilibrium model including diffusion and thermal diffusion [12].
E,F-range of evolution of the B curve when maximizing the thermodynamic experimental uncertainties [16].