PROCEEDINGS OF THE
NINTH INTERNATIONAL CONFERENCE ON

CHEMICAL VAPOR DEPOSITION

1984

PROCEEDINGS OF THE
NINTH INTERNATIONAL CONFERENCE ON

CHEMICAL VAPOR DEPOSITION
1984

Edited by

McD. Robinson
Epsilon Technology, Inc.
Tempe, Arizona

C. H. J. van den Brekel
Philips Research Laboratories
Eindhoven, The Netherlands

G. W. Cullen
RCA Laboratories
Princeton, New Jersey

J. M. Blocher, Jr.
Oxford, Ohio

P. Rai-Choudhury
Westinghouse Research and Development Center
Pittsburgh, Pennsylvania

HIGH TEMPERATURE MATERIALS,
ELECTRONICS, AND DIELECTRICS AND INSULATION DIVISIONS

Proceedings Volume 84-6

THE ELECTROCHEMICAL SOCIETY, INC., 10 South Main St., Pennington, NJ 08534-2896

Library of Congress Catalog Card Number 84-80563
Printed in the United States of America

PREFACE

This volume is the Proceedings of the Ninth International Conference on Chemical Vapor Deposition (CVD-IX), held May 7-10, 1984 in Cincinnati, Ohio, U.S.A., as part of the Spring Meeting of The Electrochemical Society.

The number of papers published here, and the geographical distribution represented, attest to the continued worldwide vitality CVD:

Denmark	1
Federal Rep. of Germany	4
Japan	2
Korea	2
Sweden	3
West Germany	4
France	6
United Kingdom	1
United States	34
USSR	1

Sixty-two papers were scheduled for presentation at the conference. Of those, 58 are represented by full length manuscripts in these Proceedings. Recently about 500 CVD papers have been published each year (see, for example, "Chemical Vapor Deposition, 1960-1980, A Bibliography", Ed. D. T. Hawkins, IFI/Plenum, N.Y. 1981). This volume therefore contains about 10% of the CVD papers that will appear this year.

We thank the authors who worked hard and patiently preparing camera-ready copy for this publication. Publication of a proceedings at the time of the conference places extra demands on the everyone because of the early deadlines. The papers were reviewed by the session chairmen and by other reviewers whom they selected. Where necessary, papers were returned to the authors for revision. In general the process of review and revision went smoothly, especially considering the demands of communicating and sending manuscripts across international boundaries. Our thanks to authors and reviewers for the superior cooperation.

The topics of these papers reflect most of the current trends in CVD. It is gratifying to see continuing progress in fundamentals: heat and mass transport, chemical kinetics and thermodynamics. Several papers address the continuing concern for defect reduction and dopant control in single crystal CVD films. Others reflect an increased interest in low temperature processing, using plasma and photon-enhanced CVD. The materials represented in these Proceedings cover most of thse to which CVD is being applied: silicon, germanium, III-V and II-VI semiconductors, metals, silicides, superconductors, magnetic and optical materials, and hard and protective coatings.

We would like to express our thanks to the many people who contributed to this volume, especially to the session chairmen who took on the major responsiblity for reviewing the manuscripts and communicating with the authors, Sarah Kilfoyle, Electrochemical Society Publications Editor, who was a valuable and continuing source of information and suport, and Christina Sampson, who capably managed the details of assembling the manuscripts into the final volume.

McD. Robinson
J. M. Blocher, Jr.
G. W. Cullen
P. Rai-Choudhury
C. H. J. van den Brekel

February, 1984

CVD - IX CONFERENCE ORGANIZATION

PROGRAM CO-CHAIRMEN

J. M. Blocher, Jr.

G. W. Cullen

P. Rai-Choudhury

McD. Robinson

C. H. J. van den Brekel

SESSION CO-CHAIRMEN

K. J. Bachmann

J. M. Blocher, Jr.

G. W. Cullen

L. M. Fraas

C. W. Pearce

D. T. Quinto

P. Rai-Choudhury

R. Reif

J. M. Shaw

S. C. Singhal

G. R. Srinivasan

C. H. J. van den Brekel

D. S. Williams

CONTENTS

Contents (Continued)

Contents (Continued)

Contents (Continued)

I. FUNDAMENTALS (A)

Professor Rafael Reif
Massachusetts Institute of Technology

Dr. G. R. Srinivasan
IBM General Technology Division

MODELLING OF CHEMICAL VAPOR DEPOSITION REACTORS

Klavs F. Jensen

Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN 55455

The modelling of chemical vapor deposition (CVD) reactors is reviewed with emphasis on reactors for growth of electronic materials. Fluid flow phenomena characteristic of CVD systems including free convection driven instabilities are described. The formulation of detailed species balances to account for the combined mass transfer and chemical kinetics are outlined. In addition, the development of kinetic rate expressions for CVD is discussed. The utility of CVD reactor analysis in extracting chemical kinetics from experimental deposition data is demonstrated for three particularly advantageous reaction configurations, (1) rotating disk, (2) stagnation point flow, and (3) impinging jet. Finally, the perceived future needs in CVD reactor modelling are outlined.

INTRODUCTION

Mathematical models for chemical vapor deposition (CVD) reactors relate performance variables (e.g. deposition rate and film composition) to operation conditions (e.g. reactor geometry, flow pattern, reactant concentration, and temperature profile). The model is formed by a complete and consistent set of mathematical equations which vary in complexity according to the level of detail sought in the representation. The simplest "model" is a statistical correlation of input parameters and performance variables. Such an approach is limited to a specific reactor at hand and a narrow operation region. It can neither be used to extrapolate the reactor performance to new operating conditions nor to design new reactors. Moreover, it provides little, if any, insight into the underlying physical and chemical rate processes.

CVD reactor models serve three main purposes, (i) the prediction of reactor performance for a given reactor and known chemical kinetics, (ii) the evaluation of kinetic parameters from reactor data, and (iii) the design of new reactors for a given process. (i) and (ii) have received the most attention in the CVD literature. Reactor design, to a large extent, has been limited to modification of existing configurations such as the horizontal and barrel geometries. In the following paragraphs, reactor models are reviewed with emphasis on reactors for deposition of elec-

tronic materials. Nevertheless, much of the discussion also applies to other CVD processes such as the deposition of protective coatings.

CVD REACTORS

Figure 1 illustrates conventional CVD reactors. In the horizontal, pancake, and barrel reactors the wall temperatures are usually considerably cooler than the deposition surfaces which are heated by rf coupling or quartz radiant heaters. The multiple-wafer-in-tube (or boat) reactor is a hot wall reactor where deposition also occurs on the reactor walls. The horizontal and barrel reactors are usually modelled in the same fashion since the flow geometry of the horizontal reactor is similar to that of one barrel side. However, the similarity is not present when the barrel is rotated as is often done in practice. Furthermore, buoyancy effects appear differently in the two reactors.

The Eversteijn model for horizontal reactors, the so-called stagnant layer model, is a well known exponent for the film theory modelling of horizontal reactors. Eversteijn et al. (1,2) considered a stagnant layer of fluid adjacent to the susceptor coupled with a well-mixed main flow region between the upper end of this layer and the reactor wall. The diffusion equation for transport across the stagnant layer was combined with a plug flow description of the main flow region to give the reactor model. The stagnant layer concept originated from flow visualization experiments with TiO_2 particles showing an almost particle free layer close to the susceptor which was interpreted as evidence for a stagnant layer. However, recent laser Doppler velocitimeter studies have revealed that the seed particles were driven away from the substrate by thermophoretic forces (3). Ban and Gilbert (4,5) used the same concept as Eversteijn but improved the model by considering a developing boundary layer and including thermodiffusion effects.

Several models have been based on fully developed laminar flow (6-9). However, as will be discussed in the next section, hydrodynamic and thermal entrance effects are significant in horizontal and barrel reactors. Consequently the applicability of the models is limited in reactor design and optimization. Nevertheless, they may serve a purpose in improving our understanding of the CVD processes. The most complete analysis of the barrel reactor so far appears to be given by Juza and Cermak (10). They make use of the 2D momentum, mass, and energy balances to demonstrate the development of the transverse velocity, concentration, and temperature profiles along the susceptor. Additional details of the reactor models may be found in (11) where key model assumptions are summarized for each model.

FLUID FLOW PHENOMENA IN CVD

The fluid flow has a pronounced influence on the performance of CVD reactors since the transport processes in the fluid phase regulate the