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Chemical Aspects of Electronic Ceramics Processing

EDITORS

Prashant N. Kumta

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David B. Beach

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John J. Sullivan

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Chemical Aspects of Electronic Ceramics Processing

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Chemical Aspects of Electronic Ceramics Processing

Preface

This volume contains 65 papers from a symposium entitled 'Chemical Aspects of Electronic Ceramics Processing,' held over four days at the 1997 MRS Fall Meeting in Boston. This symposium is the 'merger' of two previously held symposia, 'Non-Oxide Ceramics' and 'Metal Organic Chemical Vapor Deposition of Electronic Ceramics,' both held twice before in the Fall of 1993 and the Fall of 1995. The considerable overlap, between the two symposia, especially in the area of chemical vapor deposition of non-oxide electronic ceramics, suggested that combining the two would attract a wider audience without unduly sacrificing the focus of the symposium. The common themes in all of the research presented in this volume are the creative use of chemistry principles for ceramic fabrication and a multidisciplinary approach to materials research. Inorganic chemistry, solid-state chemistry, chemical engineering, materials science and engineering, and electrical engineering have all been skillfully combined to produce materials which will play an increasingly more important part in our lives.

As in prior years, chemical vapor deposition (CVD) continues to be a popular area of research and was the subject of approximately half of the papers in this volume. Particularly 'hot' areas of research are new and improved precursors, delivery systems for low-vapor pressure precursors, and improved processing and materials properties. Papers are evenly divided between oxide ceramics and non-oxide ceramics.

Another major theme in this volume is solution processing of films. Using several techniques and chemistries, a wide range of materials were deposited with excellent properties. This technique holds the promise of replacing many expensive high-vacuum techniques with simpler and cheaper solution chemistry routes. In addition to sol-gel and metal-organic decomposition (MOD) techniques, newer solution chemistry based techniques such as hydrothermal synthesis, electrochemical synthesis, synthesis in liquified gases, and electrospray synthesis are presented.

The types of materials described and the range of applications of ceramic materials to the field of electronics continues to increase. Highlights of these developments in electronic ceramics include: ferroelectric ceramic capacitors for ferroelectric nonvolatile random access memory (FRAM); high-dielectric capacitors for dynamic random access memory (DRAM); low-dielectric aerogels and mesoporous materials; electro-optical materials for waveguides, filters, and switches; electronic packaging and interconnects for microelectronics; wide-bandgap materials for blue LEDs and high temperature electronic devices.

The symposium consisted of eleven sessions that spanned four days, including a poster session and a joint session with the symposium entitled 'Intelligent Processing of Electronic Ceramics.' A tutorial was also organized on 'Chemical Processing and Applications of Electronic Ceramics: Chemical Vapor Deposition and Sol-Gel Processing' that was well attended. Another unique feature of this symposium was a panel discussion on 'Future Directions in Electronic Ceramics' that was very successful. It is the sincere hope of the symposium organizers that this volume will prove to be a valuable reference in the field of electronic ceramic processing.

Prashant N. Kumta
Aloysius F. Hepp
David B. Beach
Barry Arkle
John J. Sullivan

April, 1998

Acknowledgments

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Part I

**Chemical Vapor Deposition
of Oxide Ceramics**

METAL-ORGANIC CHEMICAL VAPOR DEPOSITION ROUTES TO FILMS OF TRANSPARENT CONDUCTING OXIDES

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ABSTRACT

This contribution reports the in situ growth of transparent, conducting $Ga_xIn_{2-x}O_3$ and $Zn_kIn_2O_{k+3}$ films by MOCVD (metal-organic chemical vapor deposition) techniques using $In(dpm)_3$, $Ga(dpm)_3$, and $Zn(dpm)_2$ (dpm = dipivaloylmethanate) as volatile precursors. In the former series, film microstructure in the $x = 0.4 - 1.0$ range is predominantly cubic with 25°C electrical conductivities as high as 1300 S/cm (n-type; carrier density = $1.2 \times 10^{20} \text{ cm}^{-3}$, mobility = $68 \text{ cm}^2/\text{Vs}$) and optical transparency in the visible region greater than that of ITO. In the latter series, films in the composition range $k = 0.16 - 3.60$ were studied; the microstructural systematics are rather complex. Electrical conductivities (25°C) as high as 1000 S/cm (n-type; carrier density = $3.7 \times 10^{20} \text{ cm}^{-3}$, mobility = $18.6 \text{ cm}^2/\text{Vs}$) for $k = 0.66$ were measured. The optical transparency window is significantly broader than that of ITO.

INTRODUCTION

Transparent conducting electrodes are key components of numerous display technologies. At present, coatings of In_2O_3 doped with Sn ("ITO") are employed on a massive scale for this purpose [1,2], although neither the electrical conductivity nor optical transparency window are truly optimum for current or envisaged device technologies. Improved materials as well as a better fundamental understanding of film growth - processing - microstructure - charge transport relationships would greatly benefit this field, as would improved film growth techniques.

A recent major advance was the report by researchers at AT&T Bell Laboratories that the layered compound $GaInO_3$ (monoclinic β - Ga_2O_3 structure) can be doped with Sn and Ge to yield, after film growth by reactive sputtering or pulsed laser deposition (PLD), films having transparencies exceeding those of typical ITO films and conductivities only slightly less [3,4]. In related work, the same researchers reported the growth by reactive sputtering and PLD of essentially amorphous, Sn-doped $Zn_3In_2O_6$ films having broader optical transparency windows than ITO and comparable conductivities [5]. Subsequent detailed studies at Northwestern of phase equilibria, structure, and charge transport in bulk samples reveals that the Ga_2O_3 - In_2O_3 - SnO_2 system is far richer than previously thought and that the conductive family $Ga_{3-x}In_{5+x}Sn_2O_{16}$ ($0.20 \leq x \leq 1.6$) prepared at 1250°C has a tetragonal crystal structure [6,7]. Complementary bulk structural, optical, and electrical studies of phase relationships in the In_2O_3 - ZnO system [8] revealed nine homologous layered compounds of composition $Zn_kIn_2O_{k+3}$ ($k = 3, 4, 5, 6, 7, 9, 11, 13$ and 15; prepared at 1300°C), with both resistivity and band gap increasing with k .