Handbook of Low and High Dielectric Constant Materials and Their Applications

Volume 1

Materials and Processing

Edited by

Hari Singh Nalwa, M.Sc., Ph.D.
Hitachi Research Laboratory
Hitachi Ltd., Ibaraki, Japan

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Preface

Recent developments in microelectronics technologies have created a great demand of low and high dielectric constant materials. As we know that internet is the fastest growing industry of the 21st century, the low and high dielectric constant materials are one of the keys components of the internet devices that perform transmission, communication and storage functions. The world wide market in 21st century for the computer and other high performance memories will be a few hundred billion dollars per year. The interlayer dielectric materials with a very low dielectric constant will play a crucial role in the future generation of integrated circuit devices particularly for ultra-large scale integration (ULSI) and high speed IC packaging. The shrinking metal spacing ($\sim$0.18 μm and below) in current IC devices is an indicator for a demand of low dielectric constant materials. On the other hand, materials with high dielectric constant have tremendous potential in capacitors of giga-bite scale dynamic random access memories (DRAMs). Silicon dioxide (SiO_2) which has a dielectric constant of about 4.0, is currently used in microelectronics packaging, however, materials with a much lower dielectric constant are in demand for the next generation of interconnects to reduce the transmission delay time in integrated circuits that would allow faster intrachip and interchip communications. The aim of ultrafast chip speed can be achieved by reducing the resistance of interlayer metal and by lowering the dielectric constant of interlayer dielectric material. With this emerging view, currently semiconductor industries are considering to produce copper/SiO_2 interconnects and to move towards integrating low dielectric constant materials with copper instead of aluminum interconnects. As the lower resistance is important for microprocessors and fast memory chips, the DRAM manufactures will move towards implementing copper interconnects. The copper/low-dielectric integration approach has been targeted for 0.13 μm generation microelectronics packaging technology to increase chip speed and reduce the number of metal levels and manufacturing costs. Dielectric constant as low as 2.0 and below have been reported for fluorinated hydrocarbons, aerogels, xerogels and nanofoams but their practical applications are far from reality at this time.

High-dielectric constant materials such as $SrTiO_3$, $BaTiO_3$, $(Ba,Sr)TiO_3$, PZT and PLZT have been considered for DRAM capacitors. The thin films of these materials deposited either by sputtering, chemical vapor deposition (CVD), sol-gel or metallorganic CVD show dielectric constant between 150 to 1000. Layered perovskite $SrBi_2Ta_2O_9$ (SBT) and PZT are another potential candidates for nonvolatile ferroelectric random-access memories (NVFRAMs). Dielectric constant as high as 300,000 for polyacene quinone radical (PAQR) polymers have been reported in the literature but such materials are impratical for applications. Besides achieving either low or high dielectric constant, other material's properties such as high thermal stability, high mechanical strength, good processability and environmental stability, low thermal expansion, low current leakage, low-moisture absorption, corrosion resistant, etc., are of equal importance. Many chemical and physical strategies have been employed to get desired dielectric materials with a high performance.

This is a rapidly growing field of science—in both novel materials and their applications in future microelectronics packaging technologies. The experimental data on inorganic and organic materials with low and high dielectric constant remain scattered in the literature. It is timely, therefore, to consolidate the current knowledge on low and high dielectric constant materials into a single reference source. This book is aimed to bring together under a single cover all low and high dielectric constant materials currently studied in academic and industrial research by covering all aspects of inorganic and organic materials from their synthetic chemistry, processing techniques, physics, structure-property relationship to applications in IC devices. Fully cross-referenced, this book will have clear, precise, and wide appeal as an essential reference source for all those interested in low and high dielectric constant materials.

Considerable efforts have been made to develop new low as well as high dielectric constant materials for applications in microelectronics industries and this book is a focal point of current research and developments in this field of science and engineering. This book has been written by the leading authorities working in academia, industries, and governmental laboratories. The book has been divided into two volumes: Volume 1 summarizes different types of low and high dielectric constant materials; whereas, Volume 2 discusses their processing, physical properties and applications. Each chapter is self-contained and fully cross-referenced to relate any given structure-property relationships. The review chapters have been organized to create continuity and cohesiveness for the topics. Low dielectric constant materials for interlayer dielectrics have been discussed by Treichel et al. Kumta and Kim have described low dielectric constant glasses and glass-ceramics for electronic packaging applications. Low-*k* amorphous carbon films for interconnections of sub-micron-scale devices have been summarized by Endo and Matsubara. Snow and Buckley wrote an overview on the cyanate ester resins with low dielectric properties and applications. Synthesis, processing, and dielectric properties of epoxy resins have been reviewed by Ichiro Ogura. The chemical mechanical polishing (CMP) of organic polymer materials for IC applications were discussed by Towery and Fury. The dielectric spectroscopy of crysralline polymers and blends has been reviewed by Kalika. Metallophthalocyanines are known for their very high thermal and chemical stability and architectural flexability. The dielectric properties of various phthalocyanines have been summarized by Phougat, Vasudevan, and Nalwa. Synthesis of various types of dielectric ceramic materials have been discussed by Nanni, Viviani, and Buscaglia. Properties of ferroelectric materials based on lead titanate have been reviewed by Pardo and coworkers. The dielectric behavior in liquids: critical mixtures and liquid crystals have been summarized by Thoen and Bose. This volume focuses on different types of dielectric materials that would help readers in getting basic knowledge of low and high dielectric constant materials.

The processing, phenomena, properties, and applications of dielectric materials are included in Volume 2. The rapid photothermal processing of dielectric materials has been discussed by Singh and Prihar. Many physical and dielectric properties are effected by the size of the grains and size effects in ferroelectric ceramics have been written by Akdogan, Leonard, and Safari. The physical and metallorganic chemical vapor deposition of ferroelectric thin films for non-volatile memories have been reviewed by Auciello, Foster, and Ramesh. Electrical aging and breakdown in dielectric materials have been discussed by Blaise and Sarjeant. Ploss discusses the pyroelectric and nonlinear dielectric properties of copolymers of vinylidene fluoride and trifluoroethylene. Dielectric spectroscopy of polar and nonpolar polymers have been described by Das-Gupta and Scarpa. An excellent overview of polymer laminate structures have been provided by Sarjeant and his colleagues. The piezocomposite design, manufacture and applications have been discussed by Tressler and Howarth. The science and technology of capacitors have been discussed by Sarjeant and coworkers. The microwave applications of ceramic dielectrics have been summarized by Penn and Alford.

I hope these two volumes will be stimulating for chemists, solid-state physicists, materials scientists, polymer scientists, ceramists, chemical and electrical engineers, professional researchers in semiconductor industries, upper-level undergraduate and graduate students in universities, individual researchers involved in microelectronic packaging and DRAM technology. This book provides, for the first time, a complete coverage on low and high dielectric constant materials, their processing, spectroscopy, properties, and applications in the field of semiconductor technology.

I have the greatest appreciation for the authors for their timely efforts and valuable information they have provided in writing these outstanding contributions in the field of their expertise. I am very grateful to Dr. Akio Mukoh and Dr. Shuuichi Oohara at Hitachi

Research Laboratory, Hitachi Ltd., for their kind support and encouragement. I would like to express my sincere gratitude to Professor Seizo Miyata of the Tokyo University of Agriculture and Technology, Professor G. K. Surya Prakash, Professor Toshiyuki Watanabe, K. P. Raghuvanshi, Rakesh Misra, Deepak Singal, Yogesh, Jagmer Singh and Ranvir Singh Chaudhary, and Ashish Kumar as well as other colleagues and friends who have supported my efforts in completing this book. I would like to acknowledge the continuous moral support and encouragement of my parents Kadam Singh, Sukh Devi, my wife Dr. Beena Singh Nalwa, and love of my kids, Surya, Ravina and Eric in this exciting enterprise.

Hari Singh Nalwa

About the Editor

Dr. Hari Singh Nalwa has been working at the Hitachi Research Laboratory, Hitachi Ltd., Japan, since 1990. He has authored over 150 scientific articles in refereed journals, books, and conference proceedings. He has 18 patents either issued or applied for on electronic and photonic materials and their based devices. Dr. Nalwa has published 18 books, including *Ferroelectric Polymers* (Marcel Dekker, 1995), *Handbook of Organic Conductive Molecules and Polymers, Volumes 1–4* (John Wiley & Sons, 1997), *Nonlinear Optics of Organic Molecules and Polymers* (CRC Press, 1997), *Organic Electroluminescent Materials and Devices* (Gordon & Breach, 1997), *Handbook of Low and High Dielectric Constant Materials and Their Applications, Vol. 1–2* (Academic Press, 1999), *Advanced Functional Molecules and Polymers, Vol. 1–4* (Gordon & Breach, 1999), and *Handbook of Nanostructured Materials and Nanotechnology, Vol. 1–5* (Academic Press, 1999).

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He is a member of the American Chemical Society (ACS) and the American Association for the Advancement of Science (AAAS). He has been awarded a number of prestigious fellowships in India and abroad that include National Merit Scholarship, Indian Space Research Organization (ISRO) Fellowship, Council of Scientific and Industrial Research (CSIR) Senior fellowship, NEC fellowship, and Japanese Government Science & Technology Agency (STA) fellowship. Dr. Nalwa has been cited in the *Who's Who in Science and Engineering, Who's Who in the World*, and *Dictionary of International Biography*. He was also an honorary visiting professor at the Indian Institute of Technology in New Delhi.

He was a guest scientist at Hahn-Meitner Institute in Berlin, Germany (1983), research associate at University of Southern California in Los Angeles (1984–1987) and State University of New York at Buffalo (1987–1988). He worked as a lecturer from 1988–1990 in the Tokyo University of Agriculture and Technology in the Department of Materials and Systems Engineering. Dr. Nalwa received a B.Sc. (1974) in biosciences from Meerut University, a M.Sc. (1977) in organic chemistry from University of Roorkee, and a Ph.D. (1983) in polymer science from Indian Institute of Technology in New Delhi, India. His research work encompasses ferroelectric polymers, electrically conducting polymers, electrets, organic nonlinear optical materials for integrated optics, electroluminescent materials, low and high dielectric constant materials for microelectronics packaging, nanostructured materials, organometallics, Langmuir-Blodgett films, high temperature-resistant polymer composites, and stereolithography.

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Chapter 1

LOW DIELECTRIC CONSTANT MATERIALS FOR INTERLAYER DIELECTRICS

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1. THE NEED FOR LOW DIELECTRIC CONSTANT (LOW-ε_r) INTERLAYER DIELECTRICS

Scaling down the feature sizes in microelectronic circuits has shown efficiency in improving circuit performance and increasing yield at lower cost per function on chip. Circuit

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speed increases are primarily due to reduction in transistor gate lengths, resulting in faster transistor switching times. As dimensions are scaled to the submicrometer range, the signal run-time delays caused by the higher resistance–capacitance (RC) product of the metallization may overcome the benefits of a decreased gate length. Based on a typical complementary metal oxide semiconductor (CMOS) inverter circuit scheme, Bothra et al. [1] derived an analytical expression for the dependence of signal risetime on the technological parameters. Their main result is that a higher interconnect performance or less switching delay can be achieved by introducing materials with higher electromigration resistance for the interconnects and by the use of lower dielectric constant insulators. For a 0.25-μm technology at a median interconnect length of 1000 μm, the authors predict a switching delay improvement of a factor of 2 for a material with $\varepsilon_r = 2$ compared to the usage of SiO_2 as an insulator.

Advanced metallization schemes need to maintain the performance benefits of scaling down device dimensions into the sub-0.5-μm regime (see Fig. 1).

Murarka [2] and Ting and Seidel [3] predict the need for a dielectric constant of $\varepsilon_r = 3$ for 0.25-μm minimum interconnect space and $\varepsilon_r = 2$ for 0.18 μm, because the use of traditional dielectrics at very small interconnect dimensions would degrade signal propagation speed and increase power consumption and cross talk.

Symposia sponsored by SEMATECH, Materials Research Society, and SRC are held regularly. The Semiconductor Industry Association (SIA) roadmap [4] discusses the need for low-ε_r materials to meet the capacitance requirements of projected increases in the clock frequency of future device generations. Their Potential Solutions Roadmap lists low-ε_r dielectric chemical vapor deposition (CVD) as the preferred technology path, with prototype tools in place by 1997. Murarka also states the attractiveness of CVD deposition of polymers [2].

SEMATECH has an active program to pursue low-ε_r materials development. Under their sponsorship, the U.S. semiconductor industry has devised a list of requirements for new low-ε_r materials [3]. These requirements require extensive integration and reliability testing in addition to the standard film characterization techniques. As recently as 1992, only a small number of integrated circuit (IC) manufacturers expressed more than a passing interest in low dielectric constant materials for intermetal dielectric applications, since the

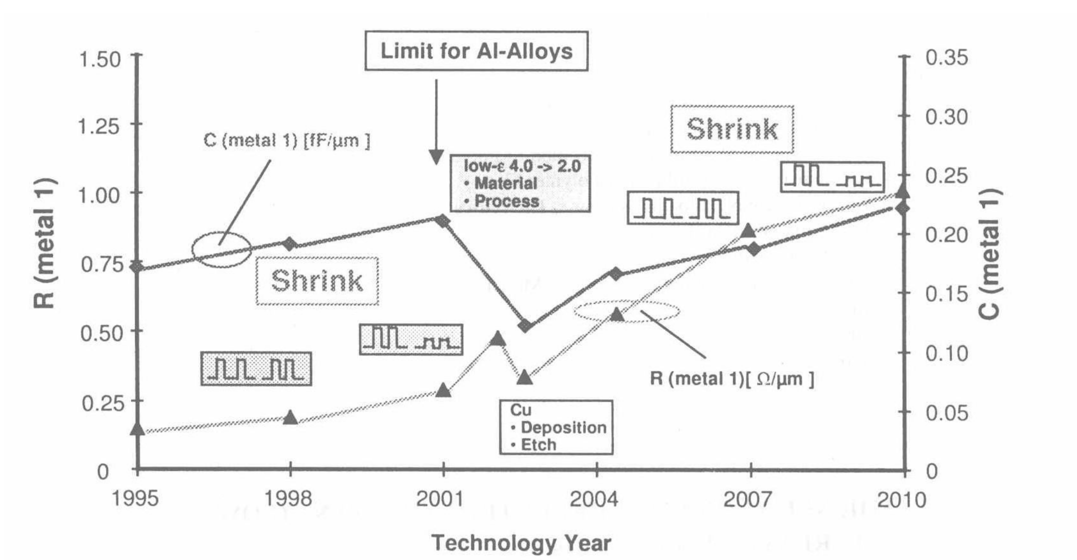

Fig. 1. Line resistance and capacitance as a function of the corresponding technology year.