

Dielectric Science and Technology

by Bill Brown, Dennis Hess, Vimal Desai, and M. Jamal Deen

The Dielectric Science and Technology (DS&T) Division celebrated its 60th anniversary in 2005 as a division within The Electrochemical Society (ECS). As with other Divisions, DS&T provides a forum for its members to exchange scientific ideas through sponsored and co-sponsored symposia, publication of papers, and other activities. The objective of the Division as was stated in 1952 by its chair, T. D. Callinan, is "to promote the attainment and dissemination of knowledge of dielectrics, including the electrical, mechanical, and chemical properties of nonconductors of electricity." Thus, a multidisciplinary approach is necessary to develop a fundamental understanding of dielectric materials, of the processes necessary for their preparation, and of their performance and reliability in their various applications.

What is a Dielectric? An Historical Perspective

The science of dielectrics, which has been pursued for well over one hundred years, is one of the oldest branches of physics and has close links to chemistry, materials, and electrical engineering. The term dielectric was first coined by Faraday to suggest that there is something analogous to current flow through a capacitor structure during the charging process when current introduced at one plate (usually a metal) flows through the insulator to charge another plate (usually a metal). The important consequence of imposing a static external field across the capacitor is that the positively and negatively charged species in the dielectric become polarized. Charging occurs only as the field within the insulator is changing. Maxwell formulated equations for electromagnetic fields as they are generated from displacement of electric charges and introduced dielectric and magnetic constants to characterize

different media. It is generally accepted that a dielectric reacts to an electric field differently, compared to free space, because it contains charges that can he displaced. Figure 1 illustrates some of the charge configurations and their response (polarization) under the influence of an external field. Because almost all material systems are made up of charges (an exception being neutron stars!), it is useful to characterize materials by their complex dielectric response function, $\mathbf{\epsilon}(\mathbf{k},\omega)$, given by

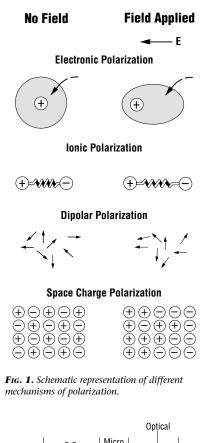
 $\mathcal{E}(\mathbf{k},\omega) = \mathcal{E}'(\mathbf{k},\omega) + i\mathcal{E}''(\mathbf{k},\omega)$

where **k** is the wave vector and ω is the frequency. The time-dependent properties, such as dielectric relaxation, can be obtained by Fourier transformation of $\mathcal{E}(\mathbf{k},\omega)$.

A schematic representation of the real part of ε is shown in Fig. 2. At high frequencies ($f > 10^{14} \, \text{s}^{-1}$), the contribution comes solely from electronic polarization, implying that

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only free electrons, as in metals, can respond to the electric field. That is why metals are such good optical reflectors! For nonequilibrium phenomena, the combination of Maxwell's equations and the continuity equations show that the conductivity tensor, σ , is related to the dielectric tensor, **E**. Even the various thermal and mechanical properties, such as thermal expansion, bulk modulus, thermal conductivity, specific heat, and refractive index, are related to the complex dielectric constant, because they depend on the arrangement and mutual interaction of charges in the material. Thus, the study of dielectrics is fundamental in nature and offers a unified understanding of many other disciplines in materials science.



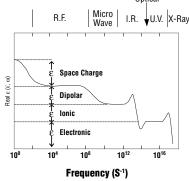


Fig. 2. Contributions to the frequency-dependent dielectric constant from the different charge configurations.

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The Scope of Dielectric Science and Technology

Although during its more than 60 years of existence, the focus of the Division has broadened according to the concerns of its active members, the materials of interest have been primarily the traditional dielectric films used in semiconductor devices and capacitors, particularly oxides and nitrides. However, more recently, materials of unique dielectric responses have been studied and utilized in novel ways.

For instance, in the not too distant past, polymer scientists and technologists expanded their horizons from consumer products to the high technology arena. Particularly notable are inventions in telecommunications, where plastic fibers are used for short optical data links, and polymeric films with large third-order susceptibility (χ^3) are used for nonlinear optics applications. In the field of microelectronics, radiation sensitive polymers (photoresists) have been formulated for use with a wide variety of exposure systems, from the early ones using visible light to those using near ultraviolet, laser, e-beam, and X-ray sources, for the fabrication of the sub-micrometer structures of high speed, high density integrated circuits. Steady progress has also been made in the field of passivation, where various polymeric films are applied to microscopic objects such as integrated circuits and the packages that house them

Ceramists have also extended the range of applications; ceramic materials are used in packages for semiconductor integrated circuits, as well as in automobile engines, in composites for aerospace vehicles, and in high efficiency power generation stations. A notable advance was the discovery of superconductivity in the Ba-La-Cu-O family of oxides, for which Bednorz and Muller were awarded the Nobel Prize in Physics in 1987.

Electronic and optical engineers are pushing the limits of the material properties and applications of organic and inorganic conductors, semiconductors, and insulators. One example is the revived interest in diamond and diamond-like films. These recent efforts resulted in higher speed, higher density devices and interconnection schemes, both electrical and optical, for computers and telecommunication systems. Another example, the low-dimensional (d = 1, d = 1)2) nanostructures, which could only be speculated about in the past, are now a reality. This allows researchers to test such fundamental concepts in quantum

mechanics as localization, electron concentration, and tunneling. It is probable that more innovative devices will follow.

Since the mid-1990s, the microelectronics industry has invested heavily, with some success, in the development of high- and low-k dielectrics (k is the dielectric constant of a material). These materials are required because of the continuing reduction of both horizontal and vertical dimensions of integrated circuits (ICs), which results in an increase of the gate leakage current, and consequently, an increase in heat dissipation. Therefore, high-k materials are needed for the gate dielectric in complementary metal-oxide-semicon ductor (CMOS) ICs, storage capacitors, and nonvolatile static memory devices. Similarly, the reduction in spacing of metal interconnects in both the vertical and horizontal dimensions has created the need for low-k materials that serve as interlevel dielectrics to offset the increase in signal propagation time between transistors, known as RC delay (R is metal wire resistance and C is interlevel dielectric capacitance). As a result of these requirements for present and future sub-100 nm IC technologies, many new dielectric materials and material combinations have been and must continue to be created and characterized if the device density of ICs is to continue to increase as anticipated by Moore's Law.

The previous discussion is not intended to suggest that dielectric science and technology is only important for electronic components. Far from it; dielectrics play important roles in applications ranging from sensors, isolation for conductors in the power utility industry, to ceramic cookware. Further, in the rapidly emerging field of biological systems, the dielectric constant is important because electrostatic effects are used to link structure and function of biological molecules. It has been proposed that electrostatic effects play a major role in important biological activities such as enzyme catalysis, electron transfer, proton transport, ion channels, and signal transduction. It is expected that the DS&T Division will play an increasing role, in collaboration with other divisions in ECS, in promoting the varied and important role of the science and technology of dielectrics in existing fields of sensors, nanotechnology, electronics, photonics, chemical and mechanical systems, but also in emerging fields of biology and biochemistry. Thus, it appears inevitable that the dielectric properties of nanoscale materials and structures will be critical to developing novel devices for current and future commercial applications.

Table I. Core Areas of Dielectric Science and Technology

Physics/Chemistry/ Materials Science

- Polarizability, Relaxation, Ions, Breakdown Phenomena
- Elementary Excitations: Polaritons, Excitons, Polarons, Phonons
- Phase Transitions, Critical Phenomena
- Bonding, Ionicity, Crystal/Ligand Fields, Electronic Correlation
- Reaction, Kinetics, Transport, Energetics, Thermodynamics
- Interfaces, Interphases

Properties of Dielectrics

- Structural/Mechanical
- Thermal
- Electrical
- Optical
- Magnetic
- Chemical

Synthesis/Processing

- Deposition: Chemical Vapor Deposition CVD, Plasma-CVD, Room Temperature (RT)CVD, Physical Vapor Deposition (PVD), Sputtering. Evaporation, Dip/Spin/Spray Coating
- Growth: Thermal, Anodic, Epitaxial
- Chemical Mechanical Planarization (CMP)
- Lithographic Processes: Photon/ Election/Ion Beam Exposure, Resist Materials
- Etching: Wet Chemical, Plasma, Reactive Ion, Ion Beam Milling Characterization
- Analytical Tools
- Modeling Manufacturing
- Monitoring/Control
- Yield
- Statistical Analysis

Reliability

- Failure Mode Analysis
- Performance Prediction
- Quality Assurance Applications
- Structural/Transportation
- Microelectronics/Optoelectronics
- Corrosion and Passivation
- Energy Production and Storage

For example, large amounts of energy can be stored in nanocomposites that show large polarizabilities. In addition, dielectric materials such as ferroelectric and piezoelectric nanomaterials offer significant advantages for communication devices and data storage systems. Recently, there have been investigations of nanoporous composites formed by the incorporation of nanosize air bubbles, leading to a significant decrease in the dielectric constant and the ability to vary the dielectric constant by controlling the concentration of air bubbles. Furthermore, the continuing trend in miniaturization requires increasingly thinner dielectric materials without nanoscale defects. An understanding of material and interfacial properties at the nanoscale is often facilitated by materials modeling as well as the development of innovative characterization tools. One such tool is the development of the scanning nonlinear dielectric microscope (SNDM) that can be used to measure the microscopic point-to-point variation of the linear and nonlinear dielectric properties of insulators.

Future requirements and achievements in the area of dielectrics can be realized only by the further development and fundamental understanding of reliable material synthesis, processing, and characterization technologies, making it possible to tailor dielectric materials, their thin film structures, and their interfaces to specific applications. In the past, these technologies have been successfully applied in the microelectronics and other industries that depend on the unique mechanical, optical, chemical, and electrical properties of high performance dielectric materials. The advent of nanoscale devices in recent years demands that scientists and engineers continue to focus attention on dielectric material design, synthesis, and characterization for enhanced performance, reliability, and manufacturability. Table I lists many of the core technology areas of interest to those involved in dielectric science and technology.

Figure 3 is an attempt to depict the multitude of interactions among the many and diverse core areas of

Table II. Symposia

- Automated IC Manufacturing
- Chemical Mechanical Polishing
- Chemical Vapor Deposition
- Copper Interconnects, New Contact Metallurgies/Structures, and Low-*k* Interlevel Dielectrics
- Diamond and Diamond-Like Films
- Dielectric Breakdown
- Dielectrics and Annealing for Compound Semiconductors
- Dielectrics for Nanosystems: Materials Science, Processing, Reliability, and Manufacturing
- Electroceramics and Solid State Ionics
- Electrochemical Processing in ULSI Fabrication
- Electrochemical Sensors for Biological Applications
- Emerging Technologies in Nanoelectronics
- Epitaxial Growth of Functional Oxides
- High Density, High Performance Cables and Connectors
- High T_c Superconductors
- High Temperature Dielectrics
- High Temperature Sensors
- Interconnection and Contact Metallization for ULSI
- Interfaces in Electronics Materials
- Low and High Dielectric Constant Materials: Materials Science, Processing, Manufacturing, and Reliability Issues

dielectric science and technology that present challenging possibilities for the community of scientists, engineers, and technologists in research, development, and manufacturing. To foster advancements in these areas and to honor technical achievements, the Division annually presents the Thomas D. Callinan award in recognition of

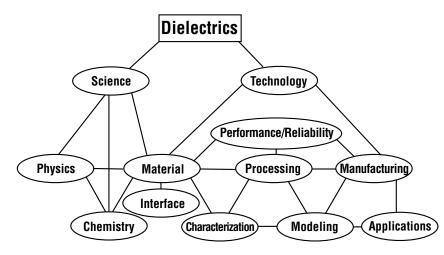


FIG. 3. Interactions among the core areas of Dielectric Science and Technology.

- Low Dielectric Constant Polymeric and Thin Film Materials
- Loss Temperature Electronics, Materials and Processing
- Metallized Plastics
- Multilevel Metallizations
- · Nanoscale Devices and Materials
- · Patterning Science and Technology
- Physics and Chemistry of ${\rm SiO}_2$ and the ${\rm SiO}_2$ Interface
- Plasma Processing
- Polymeric Materials for Integrated Circuits
- Protective Coatings at Elevated Temperatures
- Reaction Layers on Light Metals and Intermetallic Layers
- Reliability of Semiconductor Devices and Interconnections
- Science and Technology of Dielectrics in Emerging Fields
- Silicon Nitride and Silicon Oxide
- Silicon Materials Science and Technology
- State-of-the-Art Program on Compound Semiconductors
- Thin Film Materials, Processes, and Reliability: Patterning of Low- and High*k* Films and Damage Control in ULSI Device Fabrication
- ULSI Science and Technology

outstanding scientific and technical contributions to dielectrics research.

Within ECS and over the past many years, the interests of the Division have been addressed by the sponsorship or cosponsorship with other Society Divisions of symposia such as those listed in Table II.

Additional Reading

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Acknowledgment

The material for this overview was taken from three Society publications: *A History of The Electrochemical Society: 1902-1927*, past issues of *Electrochemistry and Solid-State Science in The Electrochemical Society*, and *Interface*, fall 1995. Helpful comments by Stanley I. Raider, IBM, are gratefully acknowledged.

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