BOOK REVIEWS

New Characterization Techniques for Thin Polymer Films

Edited by H. M. Tong and L. T. Nguyen, Wiley Interscience Publication, New York, NY, 1990, 368 pp., $65.00

Polymers have found a wide range of applications in microelectronics and optoelectronics. As a result, techniques to characterize these polymers in a thin-film form have proliferated. This book assembles a great number of such specialized techniques and analyses, each in detail. The editors have grouped the chapters according to their relevance to either bulk (Chapters 1 through 10) or interface (Chapters 11 through 13).

Under bulk properties, the topics include microdielectrometry, bending-beam technique, X-ray diffraction, laser interferometry, ion-beam analysis, fluorescence redistribution after pattern bleaching, surface sensors, photothermal analysis, and thermally simulated discharge current technique. Under interface properties, X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIM), Auger electron spectroscopy (AES), scanning tunneling and atomic force microscopes and adhesion studies by the indentation technique are discussed.

All of the chapters are authored or coauthored by individuals renowned for the development or current use of the associated techniques. Hence, the compiled information is up-to-date and comprehensive. Most chapters clearly demonstrate lucid writing and systematic organization. The level of the text is suitable for graduate students or industrial researchers interested in an overview and review of the particular subject matter, the technique and its application to solving characterization problems found in polymer thin films. In short, each chapter is a unique capsule and can be read alone without reference to the rest. Therefore, the most distinctive contribution of this book is the very fact that such a large number of chapters have been assembled in one place, making the book itself a handy reference for those involved in using or developing polymers for the microelectronics industry.

Upon closer examination of the chapters, one can group the topics in a different manner. Microdielectrometry and thermally stimulated discharge current are somewhat related. The former gives the dielectric spectra as functions of temperature, frequency and time. It is useful for identification of transitions, monitoring of cure and moisture uptake, and detection of ionic impurities. The latter is particularly suited for detection of thermally induced changes in films. Bending beam, X-ray diffraction, and a major part of surface sensors deal with the issue of stress in thin films. These chapters are especially well organized. Laser interferometry and Piezo-electric resonators find many applications in kinetic studies of film swelling and dissolution. As tools *per se,* they are complementary. Generically, ion-beam analysis, XPS, SIMS, and AES are related in concept and experimental design. However, the ion-beam analysis chapter is nicely tied to the photobleaching chapter via the common theme of diffusion (polymer-polymer and dopant-in-polymer). Both are then somewhat related to the subjects covered in the photothermal analysis chapter where laser-induced transient heat source, combined with acoustic and thermal detection schemes, enable the measurement of properties such as thermal conductivity of thin films. Perhaps the only two chapters that stand alone are the scanning tunneling and atomic force microscopes and adhesion by indentation technique. These, nevertheless, fall in the general domain of thin-film characterization, and their connection to the main body of the book does not appear tenuous.

The strengths of this book are the neatly-organized and lucidly-written packages of individual topics, with common interconnecting threads. The weaknesses of the book are to be found not in what is presented, but rather in what is missing. This volume could be greatly improved if a vibrational spectroscopy chapter (surface IR and Raman) were included. In addition, nonlinear optics (second harmonic generation) and angle-resolved laser light scattering could potentially be added to benefit the reader.

Despite these few misses, the editors and authors are to be commended for their excellent effort and contribution to the chemical/material science literature in polymer thin-film characterization.

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Clathrate Hydrates of Natural Gases

By *E. Dendy Sloan, Jr., Marcel Dekker, Inc., New York, 1990, 664 pp., $125.00 (U.S. and Canada), $150.00 (other countries).*

It is a comprehensive monograph on gas hydrates. Publication of this book is appropriate and timely for two reasons. First, significant research has been done on natural gas hydrates in the last several decades, which needed a compilation. Secondly, there is renewed interest in gas hydrates as a potential, future untapped resource for natural gas. This book is a valuable addition to the literature on hydrates and will serve as a single treatise for both industrial practitioners and hydrate researchers. The book ties together fundamental, theoretical concepts, and experimental advances that have emerged (primarily) during the last half century. The book includes the compilation of most of the experimental data on hydrate thermodynamic and transport properties

and phase equilibria data (collected) since 1934. The book is well edited and organized into eight chapters. Two appendices provide specific instructions and examples for using accompanied hydrate computer programs developed by the author and his coworkers. The book contains over 600 references, some as late as 1989.

Chapter 1 "Historical Perspective," briefly reviews major milestones of hydrate research divided into three major periods. The first period began in 1810, when Sir Humphrey Davy's discovery of gas hydrates initiated fundamental and laboratory studies mostly as scientific curiosity. The second period started in 1934, when Hammerschmidt observed that gas hydrate formation caused plugging of natural gas transmission lines. The third period began in mid-1960's, when it was discovered that gas hydrates occur naturally underneath permafrost in the oil- and gas-rich areas of the arctic and subarctic, and in ocean beds. This spawned a greater interest in gas hydrates especially as a potential energy resource. Recently, attempts have been on mapping hydrate resources, characterization and assessment of natural gas reserves in hydrate reservoirs, understanding the origin of gas hydrates in various geological environments, and investigating methods for recovery of natural gas from hydrates. Considerable research, along with proper economics, is needed for commercial exploitation of these resources.

The first part of Chapter 2 reviews x-ray diffraction studies in detail, and describes the crystal structures of hydrates and ice, as well as their microscopic physical and chemical characteristics. Understanding of molecular structures of hydrates and characteristics of gas molecules in the enclathrated form is essential for explaining their macroscopic behavior. Second section of this chapter compares spectroscopic, mechanical and transport properties of ice and hydrates, which are important not only for designing of experiments and analysis of data but also for locating hydrates in permafrost regions.

Chapter 3 discusses mechanisms and kinetics of hydrate formation. Although mechanisms for formation of hydrates are well understood, reliable quantitative kinetic data are scarce in literature. The rate of hydrate formation in gas processing equipments, pipelines and porous media is largely unknown and is the object of majority of current investigations.

Chapter 4 elucidates the hydrate phase equilibria with descriptions of the different regions of the phase diagram together with the simple techniques for phase equilibria calculations. The understanding of the concepts presented in this chapter is necessary for applications to naturally occurring hydrates and to hydrate problems in natural gas production, processing and transportation. The author introduces a simple algorithm (HYDK program) that is based on the K-value method to predict approximate equilibrium pressure–temperature relationship for natural gas mixtures. This chapter also includes an algorithm to compute water content of methane-rich natural gas in equilibrium with hydrates, which is useful particularly in natural gas processing applications. The effect of inhibitors on hydrate forming conditions and methods to compute hydrate number are discussed as well.

Chapter 5, a logical extension of Chapter 4, presents a statistical thermodynamic approach (microscopic) based on the molecular crystal structure for hydrate phase equilibria calculations. This approach represents the most accurate and the state-of-the-art method to compute multicomponent, multiphase hydrate equilibria. Most currently available hydrate phase equilibria prediction softwares are modifications of the original statistical thermodynamic model developed by van der Waals and Platteeuw (1959) and modified by Parrish and Prausnitz (1972). This chapter includes considerable amount of the author's own research along with introduction to the CSMHYD, a computer program based on the statistical thermodynamic approach. The model can be used to predict: 1. compressible three-phase equilibria (V-L_W-H or V-I-H); 2. incompressible three-phase equilibria (H-L_W-L_{HC}); 3. effect of inhibitors on 1 and 2; 4. four phase equilibria (V-L_{HC}-I-H or V-L_W-L_{HC}-H); and 5. two phase equilibria (H-V or H-L_{HC}).

Chapter 6 provides a detailed overview of experimental techniques to measure hydrate phase equilibria (above and below ice point, high-pressure systems) and hydrate thermal properties (heat capacity, heat of dissociation, thermal conductivity). The compilation of experimental data obtained between 1935 and 1989 on hydrate phase equilibria and thermal properties is very useful.

Chapter 7, "Hydrates in Earth," considers *in-situ* natural gas hydrate deposits in deep oceanic sediments and under permafrost as a potential future, unconventional natural gas resource. This chapter briefly reviews the extent and locations of natural gas hydrate deposits, geological and geochemical studies focused on determination of mechanism for formation of hydrates in earth, methods for hydrate resource identification and evaluation, and mathematical models for recovery of natural gas from hydrate reservoirs. The subject of *in-situ* occurrence of natural gas hydrates in the earth is a wide-range, multidisciplinary and multifaceted.

The final chapter considers applications of hydrate research to natural gas production and processing. Discussed here are current state-of-the-art methods for dissociation or prevention of gas hydrate formation in natural gas pipelines and processing equipments. In addition, this chapter covers methods to overcome plugging of wellbores by hydrates during drilling. This chapter is most useful for practitioners in the oil and gas industry.

Overall, this book will serve as an excellent reference on gas hydrates for chemical and petroleum engineers working in the area of gas hydrates and persons associated with natural gas processing and production operations. The strength of the book lies in Chapters 4–6 that describe fundamental theories and experimental studies on gas hydrate phase equilibria and thermal properties, and Chapter 8 that covers applications of natural gas hydrates in natural gas production and processing operations. It, however, provides a limited review on naturally occurring gas hydrates and experimental studies on hydrate formation and dissociation in porous media. Professor Dendy Sloan deserves congratulations and applauds for his arduous efforts for this well-written book. His past 15 years of hydrate research work has led to significant advancement in the area of gas hydrates.

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