book reviews

Materials for Microlithography: Radiation Sensitive Polymers

L. F. Thompson, C. G. Willson and J. M. J. Frechet (Eds.)
American Chemical Society, 1984, 496 pp., US $65.95.
ISBN 0-841-20871-9

Remarkable progress in the miniaturization of electronic devices over the past three decades promises to continue for many years. The size (area) of the chips has not changed significantly over the years, whereas the size of each element has decreased from above 20 microns in 1963 to less than 2 microns in 1983. Microlithography is the heart of semiconductor manufacture. This publication is the report of a symposium cosponsored by the Division of Polymeric Materials Science and Engineering and the Division of Polymer Chemistry at the 187th meeting of the American Chemical Society at St. Louis in 1984.

Unlike many of the publications in this series it is not just a report of a conference proceedings but is written and presented to provide the reader with a balanced view of materials used in microlithography. The present volume extends the topics presented in 'Introduction to Microlithography' (Ed. L. F. Thompson, C. G. Willson and M. J. Bowden). This latter volume is an excellent tutorial text on microlithography and in particular photo, electron beam and X-ray techniques. The present volume is rather narrower than the previous one in its coverage and focusses on radiation sensitivity of polymers, however the broader aspects of lithography are covered in three excellent introductory chapters.

The opening chapter by Everhart considers the factors which fundamentally limit the sensitivity of lithographic processes. Broers considers practical and fundamental aspects of lithography. It is of interest to note that serious attention is given to electron storage rings and justifies the bias of this volume towards photochemical processes. A broad review of resist materials for fine line lithography which is an in-depth discussion electron beam and X-ray lithography. The remaining papers are divided into two sections, fundamental radiation chemistry and resist materials and applications.

The section on radiation chemistry opens with a chapter which discusses polymer degradation by high energy radiation. Microlithography was initially very much a trial and error subject which is now seeking a more fundamental base. This excellent introduction to radiation chemistry and provides a basis for understanding the processes occurring when resist materials are subjected to high energy particle beams. The other chapters in this section deal with pulse radiolysis of chloromethylated polystyrene, a material which is being widely considered as a negative electron beam resist. The subject of photochemistry in the area of microlithography is discussed by Guillet in a review centred on ketone polymers. The subject of radiation interaction with polymers is extended in chapters dealing with radiolysis of poly(isoprpenyl t butyl ketone), laser induced polymerization, polymer bonded electron transfer sensitizers, novel synthesis and photochemical reaction of the polymers with pendant photosensitive and photosensitizer groups and novel techniques for determining radiation chemical yields of negative electron beam resists. These chapters indicate the increasing awareness of workers in the microlithography area of a need to understand the fundamental processes occurring in resist materials.

The second section of the book is concerned with resist materials and their applications and opens with a chapter on the photo-Fries rearrangement and its use in polymeric imaging systems. The emphasis in this section is upon photochemistry and topics covered include organic direct optical recording media, primary and secondary reactions in photoinitiated free radical polymerization of organic coatings, photochemistry of ketone polymers, new radiation-sensitive polymers based on polysilane derivatives, novolac resins for use in photolithography. Electron beam resist materials are not completely neglected and chapters dealing with positive weakening electron beam resists based on maleic anhydride copolymers, chlorinated polymethylstyrene, phenolic resins containing epoxy and aside compounds, alpha substituted benzyl methacrylates and ketone polymers.

This text is not only a well-edited conference report; it is also a very useful complement to the earlier publication. Polymeric materials, especially the radiation-sensitive polymers, lie at the heart of microlithography. For the first time, it will be necessary for the development engineer as well as the scientist to possess a thorough understanding of the chemistry of radiation-sensitive polymers. This book provides the foundation for such an understanding. Although the book is based on research papers presented at a symposium, it has been constructed so as to provide a tutorial text complementing the previous introductory text on this topic.

This text is strongly recommended to those interested in obtaining an understanding of microlithography as currently applied, as well as in developing the materials science which underlies this subject. Unfortunately these texts are rather expensive in the UK; although more modestly priced in the USA. Despite the price barrier I am sure that the serious worker in this research area will find this addition to the literature a necessary purchase for their library.

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Surface coatings

Swaraj Paul
J. Wiley and Sons, 1985, 741 pp, £48 ISBN 0-471-90397-3

Devoted to the science and technology of paints, the book first deals with the chemistry and industrial production of polymeric binders (310 pp), and then with pigments (64 pp), before proceeding to paints and paint properties (180 pp). Finally there is a section (175 pp) on the newer technologies, such as the modifications made during the last two decades in response to legislation in certain countries, to reduce dependency upon volatile and possibly harmful organic solvents in surface coatings.

The first chapter on the synthesis of polymeric binders briefly covers the essentials of polymerization theory in preparation for a full discussion of the chemistry of those industrial resins that are important in paint systems: alkyds and polyesters, formaldehyde systems, epoxy resins and so on. It is typical that the section on silicone resins commences with an exposition of their differences from, and advantages over, alkyl resins, and a citation of the recent relevant reviews. The type of alkyl or aryl substituent determines such paint characteristics as

gloss, hardness, flexibility, rate of cure and thermal life, and thus the method of application and purpose of use. On their own, silicones can form a clear and colourless water-repelling film over masonry, and they may be employed as straight additives to paints with another base, or, by a chemical reaction, the silicone may become covalently bound to alkyd molecules or to polyester, epoxy or acrylic resins.

The customer commonly purchases paints as much for their decorative colour as for their capacity to protect and preserve. Over the years a large range of inorganic and organic pigments have been discovered, and methods devised for their chemical production, to regulate particle size and to disperse the material with ball mills; and of course, no paint is of much use unless the surface has been properly prepared to receive it. Paul has provided a guide to the technical methods of evaluating the many properties of paints before, during and after their application, during each of which periods there is a demand for particular, sometimes conflicting, attributes. In many ways water is unsuitable as a paint carrier, yet it has certain advantages—it cannot pollute and it does not burn. Many strategies have been found for producing suitable water soluble paint resins and for maintaining stable aqueous dispersions. While standard curing chemistry has been used for water-born paints, it has been found advantageous to develop u.v. curing for the rapid and low temperature coating of production line articles. A category of paints—the high solids coatings—has recently emerged in which the solvent content is greatly reduced, and the issue of which carrier to employ has been solved altogether by the discovery and subsequent commercial realization of the technique of coating substrates by immersing them in hot air-fluidized powders.

One may carp a little about errors that will be removed in a second edition: for example, *Table 2.1* lacks the Hammet ρ parameter values that are referred to in the text, and molecular diagrams are occasionally inaccurate. There are other features that may be questioned. Curiously, Hildebrand's solubility parameter, δ, is not defined nor are values for the common paint solvents given, but Small's suggestion that the δ values of a polymer may be obtained from quantities associated with the consistuent parts is given twice, in almost the same terms, firstly when the solubility of acrylics is discussed and secondly in the context of film formation by solvent evaporation. Either such elementary ideas might have been introduced in a preliminary section, or more crossreferencing provided in the text. While the index would serve to link the various parts dealing with this topic, a search therein for the related topic 'adhesion' would fail. And what exactly are the Kauri-butanol values of mineral spirit thinners? A sense of proportion would have been created by the provision of some information on the size and value of the markets for the chief surface coatings.

The topics are generally covered thoroughly, and ample reference provided to the literature up to 1982. The examples of products and practices do not, as in some texts, overtly depend upon the commerce of any particular firm, country or continent. This reader gained an impression that the proportion of work performed in the U.K. decreased in the citations as the author moved from basic science to applied technology, but wherever the work was originally performed, the results are now comprehensively set out. Thus even those who feel that they are ahead in the field will find the book, with its references, of great relevance and assistance.

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