

SURFACE AND COLLOID SCIENCE IN COMPUTER TECHNOLOGY



Composites

**Lithographic
Materials**

Thin Films

**Dispersed
Media**

SURFACE AND COLLOID SCIENCE IN COMPUTER TECHNOLOGY

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SURFACE AND COLLOID SCIENCE IN COMPUTER TECHNOLOGY

PREFACE

This volume chronicles the proceedings of the Symposium on Surface and Colloid Science in Computer Technology held as a part of the 5th International Conference on Surface and Colloid Science, and 59th Colloid and Surface Science Symposium sponsored by the Division of Colloid and Surface Chemistry of the American Chemical Society, and the International Association of Colloid and Interface Scientists at Clarkson University, Potsdam, N.Y., June 24-28, 1985.

Computer technology has many aspects, e.g., hardware development, software development, and information processing. However, in this Symposium we were exclusively concerned with the materials considerations pertaining to microelectronics; surface and colloid science plays a very vital role in the materials aspects of microelectronics/computer technology.

A complete catalog of instances where surface and colloid science is important would be prohibitively long, so here a few eclectic examples should suffice to underscore the importance of interfacial aspects of materials in the wonderful world of computers. As for colloidal phenomena, the dispersion behavior of ceramic powders (in making the substrate on which semiconductor chip is placed) and magnetic particles (for making magnetic tapes and disks) is of critical importance. This calls for fundamental understanding of stability behavior in both aqueous and nonaqueous media, and the ways to control dispersion characteristics. On the other hand, there are myriad applications of thin films in microelectronics and irrespective of the function of a thin film, its adhesion to the underlying substrate is of cardinal importance. If the adhesion is inadequate, it leads to delamination and associated problems. So the importance of understanding interfacial interactions between different materials and of devising means to tailor these interactions is quite patent. As a matter of fact, many problems/failures can be traced to lack of compatibility or suboptimum materials interfaces.

In the case of printing, the proper ink-paper interactions are a desideratum for print quality, and surface and colloidal phenomena play an important role. Recently, there has been considerable interest in exploring new monolayer and Langmuir-Blodgett film materials for use as electron-beam resists for microlithography. Here, fundamental understanding of the behavior of L-B films, such as stability, radiation characteristics, etc. are important. This provides a challenge to the ingenuity of the synthetic chemist to come up with amphiphilic molecules with desired functional moieties. New vistas in microlithography should emerge as desired amphiphilic molecules make their presence.

So when this symposium was conceived and initial contacts made with potential contributors, there was a very gratifying response and

the consensus was that such a symposium was both timely and needed. The final symposium program contained 48 papers by authors who hailed from many and varied institutions and had different backgrounds and interests. But they all were interested in the relevance and importance of interfacial phenomena in microelectronics/computer technology. In essence, this event was truly inter-, multi- and trans-disciplinary in nature, scope, and content.

This symposium was designed to bring together scientists and technologists involved in interfacial aspects of materials germane to microelectronics/computer technology, to discover the latest developments, to provide an opportunity for cross-pollination of ideas, and to identify areas which needed intensified research efforts. If the comments from the authors and attendees are a measure of the success of an event, then this symposium was a great success. Also may I add that many attendees commented that this symposium was the first comprehensive event highlighting the importance and pervasiveness of surface and colloid science in the arena of microelectronics.

Now let me turn to this proceedings volume which contains 27 papers arranged in five parts as follows: Acid-Base Concepts and Colloidal Dispersions; Adhesion of Films and Coatings Including Resists; Adhesion Aspects of Thin Films, and Metal-Polymer Interfaces; Monolayers and Langmuir-Blodgett Films: Relevance to Microelectronics; and Interfacial Aspects in Printing. The topics covered include: importance of acid-base interactions in inorganic powder dispersions, stability of colloids in aqueous and nonaqueous media, colloidal behavior of ceramic and magnetic particles; adhesion of polymeric films, role of silanes in improving polymer-polymer adhesion, resist adhesion and the ways to improve it, stresses in thin films and relevance to adhesion, plasma polymerized films, radiation enhanced adhesion of thin films, metallized polyimides; monolayers and L-B films as electron-beam resists, microlithography, various applications of organized assemblies, magnetic monolayers; paper-ink interactions, surface energetics of papers used in printing, and paper-polymer adhesion. So the topics covered in this volume represent interfacial aspects of many and varied materials germane to microelectronics/computer technology.

It should be recorded for posterity that each paper was peer reviewed by at least two reviewers and the manuscripts were returned to the authors for suitable revisions. So the review process was an integral part of the overall editing process. As for discussion, although no formal discussion is included in this volume, there were brisk and enlightening (not exothermic) discussions, both formal and informal, throughout the symposium.

I certainly hope this proceedings volume, which I believe is the first one on this topic, will be useful to a variety of researchers. Let me mention here that this book contains both overviews and original research contributions. It should provide a source of new ideas and directions for research in surface and colloid science to make this discipline more relevant to microelectronics. Apropos, some of the current ideas, approaches and techniques (e.g., acid-base concepts in dispersions and adhesion, radiation enhancement of adhesion of thin films, fundamental understanding of interfacial interactions, etc.) should provide a quantum jump in our knowledge to enable us to select (or modify) materials so as to make them interfacially compatible.

Acknowledgements: First, I am thankful to the officials of the sponsoring organizations for their interest in this symposium. My special thanks are due to S.B. Korin (IBM Corp.) for allowing me to

organize this symposium and to edit these proceedings. I must take this opportunity to express my sincere thanks to the unsung heroes (reviewers) for their time and very valuable comments, as comments from peers are important in maintaining the quality of publications. In the end, I would like to acknowledge the patience, enthusiasm and contributions of the authors without which this book would not have existed.

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CONTENTS

PART I. ACID-BASE CONCEPTS, AND COLLOIDAL DISPERSIONS

Role of Acid-Base Interactions in Inorganic Powder Dispersions and Composites F.M. Fowkes.....	3
The Relevance of Lewis Acid-Base Chemistry to Surface Interactions W.B. Jensen.....	27
Surface Charge Characteristics of Chromium (IV) Dioxide in Tetrahydrofuran with Special Reference to Magnetic-Ink Dispersions G.F. Hudson, S. Raghavan, and D.A. Roylance.....	61
Interactions Between Polyelectrolytes and Oxides in Aqueous Suspensions J. Cesarano III and I.A. Aksay.....	73
Pressure Filtration of Monosized Colloidal Silica M. Velazquez and S.C. Danforth.....	87
Sol-Gel Routes to Ceramics and Glasses I. Gels F.J. Bonner.....	107

PART II. ADHESION OF FILMS AND COATINGS INCLUDING RESISTS

Importance of Interfaces in Microelectronic Device Fabrication J.N. Helbert, F.Y. Robb, B.R. Svecovsky, N.C. Saha.....	121
Role of Silanes in Polymer-Polymer Adhesion E.P. Plueddemann.....	143
Infrared and X-Ray Photoelectron Spectroscopy of Thin Silane Films on Iron and Titanium F.J. Boerio and D.J. Ondrus.....	155
Zirconaluminate Coupling Agents as High Performance Adhesion Promoters L.B. Cohen.....	171
Stresses in Thin Polymeric Films: Relevance to Adhesion and Fracture R.H. Lacombe.....	179
Adhesion and Crosslink Gradient in a Photoresist R.L. Geary, S.V. Babu, and J. Stephanie.....	199

PART III. ADHESION ASPECTS OF THIN FILMS AND METAL-POLYMER INTERFACES

Radiation Enhanced Adhesion of Thin Films J.E.E. Baglin.....	211
Modification of Silver/Silicon Interfaces During MeV-Ion Bombardment: The Role of an Interfacial Oxide Layer L.E. Seiberling and R.L. Headrick.....	235
Adhesion, Barrier, and Passivation Characteristics of Plasma Polymerized Organic Thin Films D.L. Cho and H. Yasuda.....	249
Nuclear Scattering Profiles of Polyimide-Metal Interfaces C. Chauvin, E. Sacher, A. Yelon, R. Groleau and S. Gujrathi.....	267
A Thermodynamic Model for Predicting Formation of Chemical Bonds Between Metals and Cured Polyimides During Metallization N.J. Chou and C.H. Tang.....	287
The Mechanism of Plasma Etching of Polymers and Its Relevance to Adhesion J.F. Evans, J.G. Newman and J.H. Gibson.....	299
Thermal Desorption Study of Physical Forces at the PTFE Surface D.R. Wheeler and S.V. Pepper.....	309

PART IV. MONOLAYERS AND LANGMUIR-BLODGETT FILMS: RELEVANCE TO MICROELECTRONICS

Properties and Applications of Well-Tailored Organized Assemblies G.J. Kovacs and P.S. Vincett.....	323
Microolithography with Monolayers and Langmuir-Blodgett Films A. Barraud.....	343
Dry Development of Monolayer-Based Electron-Beam Resists B.M.J. Kellner and G. Czornyj.....	353
Experiments on Langmuir-Blodgett Magnetic Monolayers of Manganese Stearate M.Pomerantz.....	361
Structural Modifications of L-B Films: Order-Disorder Transitions and Polymerization J.D. Swalen, J.P. Rabe, C.A. Brown and J.F. Rabolt.....	375

PART V. INTERFACIAL ASPECTS IN PRINTING

Hydrocarbon Based Inks for Electronic Printing J.M. Duff, R.W. Wong and M.D. Croucher.....	385
Effect of Surface Chemistry on the Adhesion of Thermoplastic Polymers to Paper J. Borch.....	399

Ink/Paper Interactions in Ink Jet Printing (IJP)
J.F. Oliver..... 409
About the Contributors..... 429
Index..... 439

PART I. ACID-BASE CONCEPTS, AND COLLOIDAL DISPERSIONS

ROLE OF ACID-BASE INTERACTIONS IN INORGANIC POWDER DISPERSIONS AND COMPOSITES

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The dispersion of inorganic powders into polymer solutions or polymer melts requires strong exothermic interfacial interactions between the polymer and surface sites of the powder. These interactions tend to insure attachment of polymers to the entire surface of each particle, thereby minimizing any tendency to form the clumps which are so deleterious to the performance of magnetic, dielectric, or ceramic dispersions.

The exothermic interactions of polymers with the surface sites of inorganic powders are predominantly of the Lewis acid-base type, and are predictable from measurements of the surface acidity or basicity of the powders and from measurements of the acidity or basicity of the functional sites of polymers.

Acid-base interactions of the surface sites of powders with components of the surrounding organic medium (as in a polymer melt or solution) provides strong attachments and in addition provides electrostatic potentials to the particles and consequent inter-particle repulsive interaction which promotes dispersion stability, especially when adsorbed layers also provide some degree of steric stabilization as well. The component responsible for electrostatic charging and stabilizing can be the matrix polymer or an added dispersant, but if a dispersant is used it should be compatible with the cast film.

In many practical systems the inorganic powder and the matrix polymer are chosen for their electrical or mechanical properties and they often do not have sufficient mutual acid-base interaction to provide good dispersions. A practical solution to this problem is to modify the surface of the powder so as to insure strong acid-base interaction with the matrix polymer; we have had the most success in modifying the surface acidity or basicity of inorganic powders by using carefully chosen silane coupling agents.

INTRODUCTION

In the electronics industry one of the general materials problems is how to make concentrated dispersions of inorganic particles in polymer matrices which are uniform, flexible and tough. Such dispersions are used to make polymer films with specific electrical properties provided by the inorganic powder. For instance, magnetic particles are used in magnetic memory storage media such as film or discs, conductive particles such as silver or carbon black are used to provide conductive polymers, and powders of very high dielectric constant are used to provide polymer films of high dielectric constant. In modern ceramic technology, polymer melts or solutions are heavily loaded with ceramic powders and cast or injection-molded into specific shapes for firing at elevated temperatures to drive out the polymer and sinter the powder into the same shape as the cast or extruded form. This technology has become important in manufacture of ceramic substrates for integrated circuit chips, with interconnection patterns in the ceramic which are introduced in the cast films of polymer filled with ceramic powder. The above examples are all considered polymer composites, and they all share the usual problems of composites, such as the quality of dispersion of the powder, and the strength of adhesion of the matrix polymer to the surface sites of the powder.

The bonding of polymers to inorganic surfaces involves three kinds of attractive forces: 1), the general dispersion (or van der Waals) forces which operate in all materials and between all materials; 2), the specific Lewis acid-base interactions between electron-accepting (acid) sites of one material with the electron-donating (basic) sites of another; and 3), electrostatic attractions between positively and negatively charged materials. Hydrogen bonds are also exothermic and specific, but these are only a subset of the Lewis acid-base interactions. Although the interaction of permanent dipoles with one another or with polarizable molecules is important in dense gases and was once thought to be important in condensed media, such interactions are now known to be too weak to be measurable in liquids or solids, or at interfaces¹. The exothermic nature of acid-base interactions in organic media has been illustrated in much detail by the research papers of Drago and coworkers^{2,3}, and a correlation of the negative heats of acid-base interaction ($-\Delta H^{ab}$) was developed:

$$-\Delta H^{ab} = C_A C_B + E_A E_B \quad [1]$$

allowing predictions of heats of acid-base interaction to within about 0.2 kcal/mole. In Equation [1] the acid (A) and base (B) each have two constants; the C constant relates to the covalent character of the bond and the E constant relates to the electrostatic character of the bond. Drago and co-workers used calorimetric and infrared spectral data to evaluate the E and C constants of about forty organic acids and bases, and these constants can be used to estimate the E and C constants of polymers. For instance, polymers with ester groups have about the same basicity as methyl acetate or ethyl acetate, polymers with benzene rings have about the same basicity as benzene, and polymers such as polyvinylchloride have about the same acidity as chloroform, as will be illustrated later in this paper.

The adsorption of polymers from solution onto inorganic powders has been shown to be dominated by interfacial acid-base interactions between the polymer and the surface sites of the powder⁴. Figure 1 illustrates the adsorption of a model basic powder (calcium carbonate, with basic surface sites of carbonate groups) or of a model acidic powder (silica, with acidic SiOH surface sites) in neutral organic solutions of either a model basic polymer (PMMA, polymethylmethacrylate) or a model acidic polymer (CPVC, a post-chlorinated polyvinylchloride).

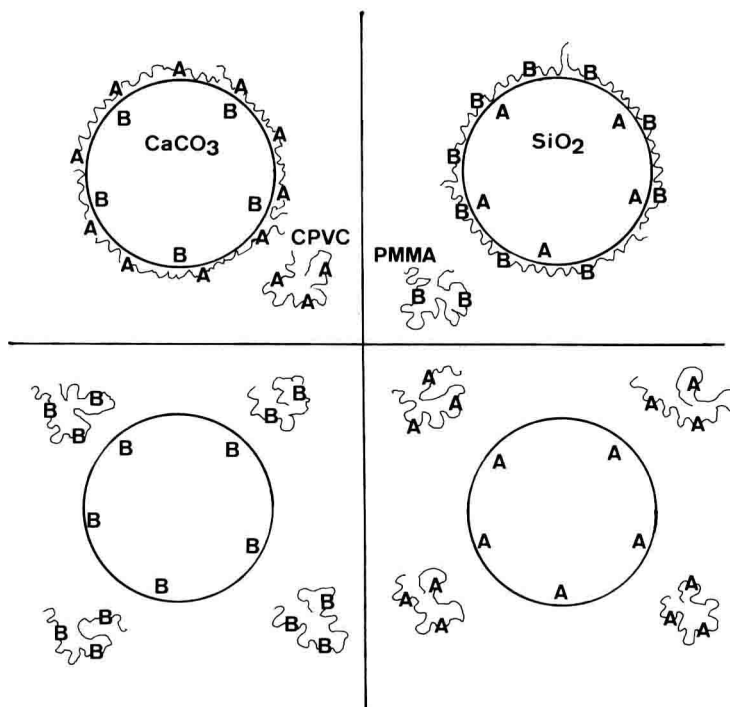


Figure 1. In neutral solvents acidic polymers such as CPVC adsorb onto the basic surface of calcium carbonate particles, but not onto the acidic surface of silica particles. Basic polymers such as PMMA adsorb only on the silica particles.

No adsorption occurred when both powder and polymer were basic, nor when they were both acidic, but strong adsorption occurred with the acidic polymer on basic powders or with the basic polymer on acidic powders. This study illustrated that dipole forces play no role in such adsorption, for both polymers have polar groups and both powders have appreciable surface polarity. We see that polar groups interact with each other only when one is acidic and the other basic. This study then concentrated on the adsorption of the basic PMMA polymer onto the acidic silica powders from a wider range of solvents, including acidic solvents such as methylene chloride and chloroform, and basic solvents such as *p*-dioxane and tetrahydrofuran (THF). In Figure 2 it is seen that the more basic solvents compete rather successfully against the basic PMMA for adsorption onto the acidic sites of silica, and that the more acidic solvents such as chloroform compete rather effectively against the acidic SiOH sites of silica for the basic sites of PMMA, thus diminishing the amount of PMMA adsorbed from either the more basic or the more acidic solvents.

The specific acid-base interactions which promote adsorption also provide strong adhesion between matrix polymers and dispersed powders. Figure 3 illustrates the stiffness (relative modulus) of films of silica-filled PMMA cast from THF, a strongly basic and competing solvent, and compares this with the stiffness of films of the same composition cast from methylene chloride, a more neutral solvent from which PMMA adsorbs strongly onto silica. It can be seen that the films cast from methylene chloride, the non-competing solvent, are much stiffer than those cast from THF, illustrating that the strong acid-base interactions which promote the microscopic phenomenon of adsorption also promote the macroscopic phenomenon of adhesion and stiffening.

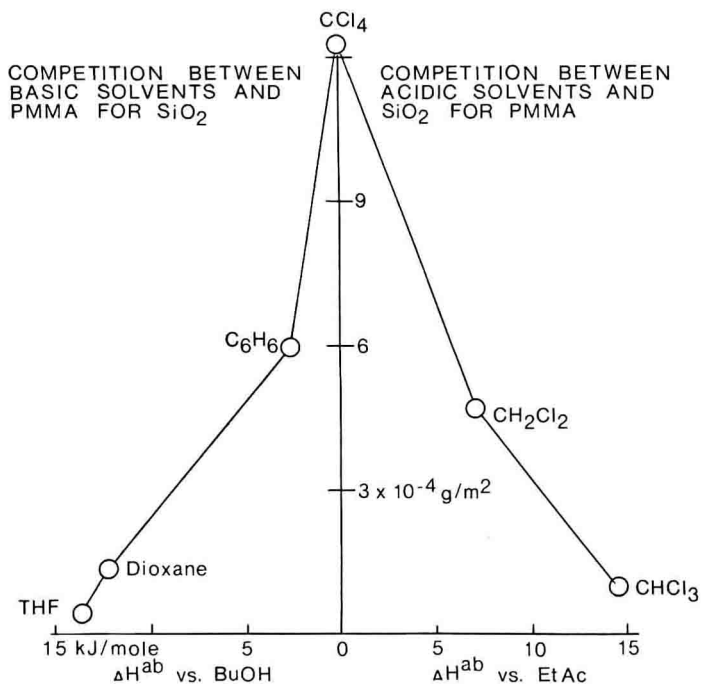


Figure 2. The acidity or basicity of solvents can appreciably reduce the adsorption of the basic polymer PMMA onto the acidic surface sites of silica⁴. Reprinted from IEC Product R&D by permission of the copyright owners, the American Chemical Society.

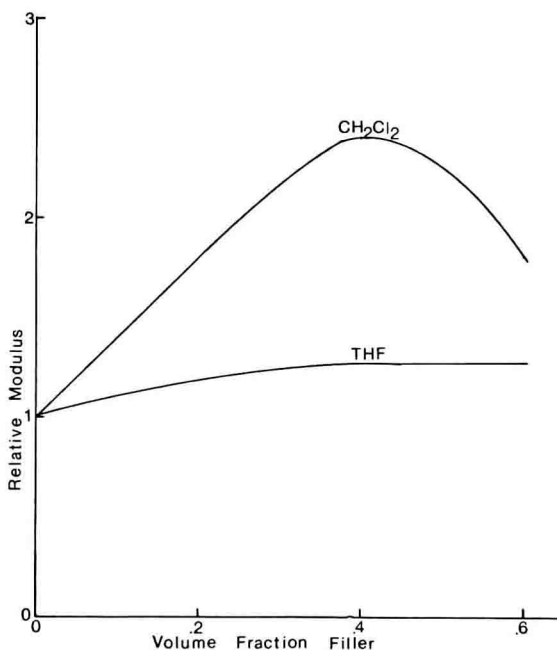


Figure 3. The stiffness of composite films of silica-filled PMMA cast from various solvents depends on the degree of adsorption of the basic PMMA groups onto the acidic surface sites of silica⁵. Films cast from the weakly competing methylene chloride are much stiffer than those cast from the strongly competing THF.

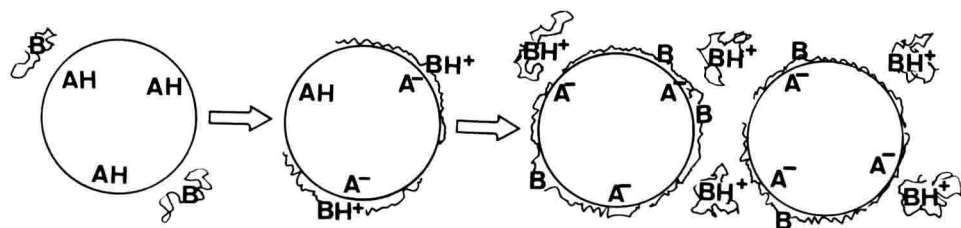


Figure 4. Proton-transfer mechanism of electrostatic charging of acidic inorganic particles in non-aqueous solutions of basic dispersants. The adsorbed basic, but uncharged, dispersant becomes charged by accepting a proton from an acidic site. However the particle becomes charged only when the dispersant concentration is high enough for the dynamic process of adsorption-desorption to desorb the charged dispersant molecules.⁶

Interfacial acid-base interactions also promote electrostatic charging of inorganic particles in organic media. This charge transfer occurs at the surface of particles, where either proton or electron transfer provides large enough surface potentials to promote dispersion-stabilizing electrostatic repulsion between particles (Fig. 4). In organic media stabilization of dispersions against flocculation generally requires both electrostatic and steric repulsion, as illustrated in Figure 5, after a text-book illustration from Shaw. Steric stabilizers provide an adsorbed film thickness of 5-10 nm, but require strong anchoring to the surface, usually by acid-base bonds. The most widely used steric stabilizers have basic nitrogen groups for anchoring, but some with carboxylic acid anchors are also readily available. The steric barriers are made up of large organic groups which should be well solvated for maximum steric repulsion. We find then that acid-base interactions at the surface of dispersed powders are a requirement for getting good stable dispersions as well as getting good electrical and mechanical properties of the resulting composite films.

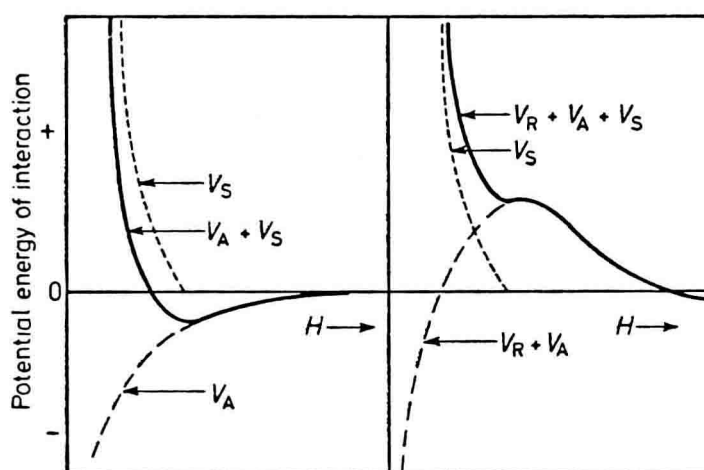


Figure 5. Left: diagram of inter-particle potential energy versus inter-particle distance for steric (V_S) repulsion and dispersion force attraction (V_A). Right: with electrostatic repulsion (V_R) added.