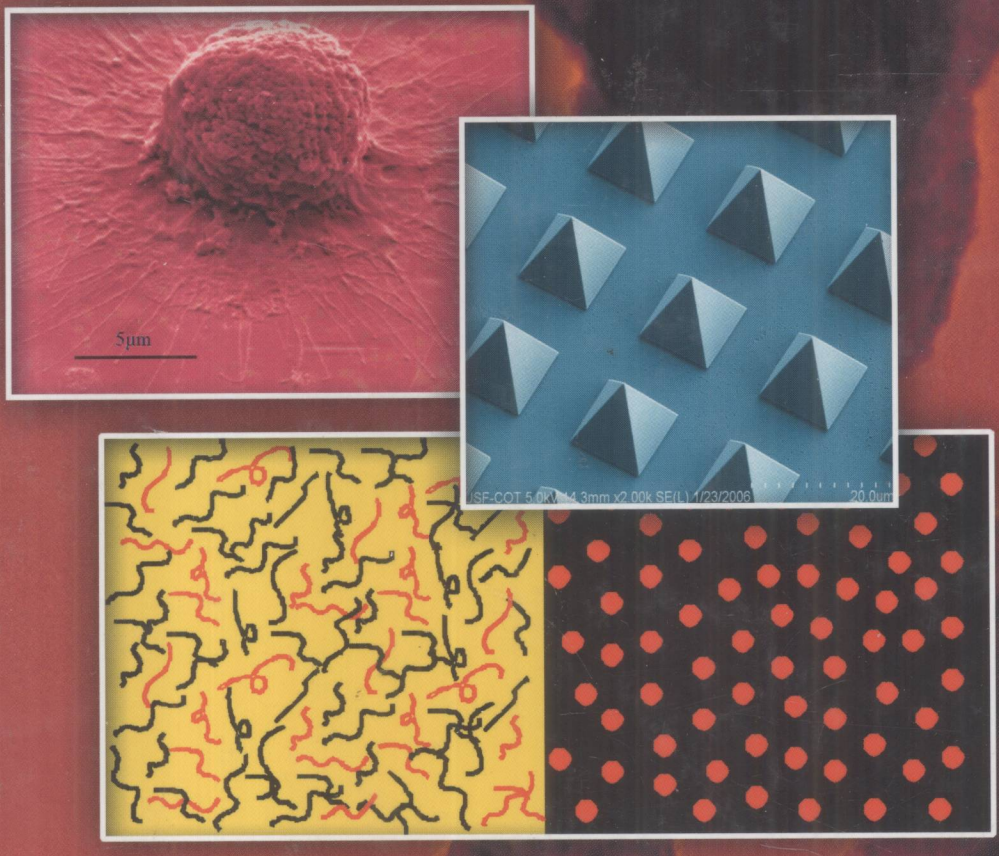
Materials Characterization Techniques



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Preface

Everything we use is made of some material or a combination of materials. We use different types of materials—metals, ceramics, polymers, semiconductors, and composites—in our daily lives. We address the scientific fundamentals of materials, their processing, and their engineering design for technological applications. We apply basic principles of chemistry, physics and biology in order to understand the structure of materials at all relevant length scales and how this structure determines its properties. We design scientific processes to fabricate materials to meet the needs of modern technology. Finally we focus on the performance of the material under specific use conditions. Perhaps, the most distinguishing feature of the discipline is the appreciation and focus on the interrelationships and interdependence between processing, structure, properties and performance. Preparation and characterization of materials form crucial and vital aspects of materials research and sophisticated instruments are now available to apply an interdisciplinary approach to understand the wide range of mutually interacting processes, mechanisms and materials.

The purpose of the book is to provide both senior undergraduates and graduate students involved in interdisciplinary research an introductory course on modern materials characterization techniques. Characterization has been one of the foundational pillars of materials science for well over a century and still many modern characterization techniques are evolving due to emergence of the nanotechnology field, this textbook provides focus on principles and applications of various instrument generally used in characterization of engineering materials.

The book evolved out of lectures given over a decade or more by each author on one or more topics covered in the book, although some materials derive from the scholarly writing for the professional community and from the author's own research activities. We are thankful to students from various disciplines whose educational needs in materials characterization served as the driving force for this book. We hope that this textbook will facilitate learning by the current and future generation of students, and in one way or the other, facilitate advancing of understanding of materials particularly that in the nanotechnology, nanomedical and nanoengineering fields.

We owe special gratitude to CRC Press for invitation to write this textbook and for their valuable help and guidance in completing this book, their patience with our pace of writing, and their encouragement at every activation barrier. We wish to thank the Nanyang Technological University, Singapore and the University of South Florida, Tampa for institutional

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Sam Zhang
Lin Li
Ashok Kumar

Contents

1

Introduction

This book grew out of materials characterization courses the authors taught over the last decade to engineering graduate students pursuing master's and Ph.D. degrees. The purpose of this book is to provide engineering graduates and senior undergraduates an introductory course on modern materials characterization techniques, especially with respect to nanotechnology, nanomedicine or nanoengineering: surface analysis, composition analysis and structural analysis using modern techniques such as x-ray, electron beam, chromatography, etc. This book makes a special effort to focus on principles and applications, leaving lengthy (and usually intimidating to engineering students) derivations and formulations out of its scope, engineering students can concentrate on the basic principles and applications of these modern technologies.

There are 11 chapters in this book. Chapter 2 deals with contact angle in surface analysis, whereas Chapter 3 concentrates on x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Originally, XPS and AES were planned as two separate chapters. However, XPS and AES have many things in common, especially in fundamentals and vacuum system. In fact, usually these two systems are physically two in one. Thus, we decided to put these two technologies into one single chapter. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) are both discussed in Chapter 4 because they have a great deal in common, especially in terms of principles. In fact, AFM can be viewed as a rough version of STM. X-ray diffraction (XRD) is an important tool to investigate crystalline structures of materials. Chapter 5 covers X-ray characteristics & generation, lattice planes & Bragg's Law, powder diffraction, thin film diffraction, texture measurements, etc. Two electron microscopic methods, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are described in Chapters 6 and 7 respectively. The principles of TEM and SEM are given in an easy to read way of understanding. Applications of TEM and SEM are also illustrated. Chapter 8 provides general principles of chromatography, classification of chromatography, separation modes and mechanisms, partition and retention. Particularly, ion exchange chromatography, gel permeation chromatography, gel electrophoresis chromatography, high-performance liquid chromatography, gas chromatography are described respectively. Finally three methods for quantitative analysis methods are explained with practical examples.

Infrared spectroscopy (IR) is introduced in Chapter 9 from the angle of molecular vibration and resonance, followed by advanced IR and Fourier transform infrared spectroscopy (FTIR). UV absorption, Beer-Lambert law, Ultraviolet/visible spectroscopy and a case study are covered in this chapter. Chapter 10 gives three kinds of methods of macro and micro thermal analyses: differential scanning calorimetry (DSC), isothermal titration calorimetry (ITC), and thermogravimetric analysis (TGA). DSC and ITC can be either macro or micro-scaled. A variety of thermal transitions and thermodynamic interactions can be determined by means of DSC or ITC. On the other hand, TGA is used to determine thermal stability or thermal reactions. In Chapter 11, the fundamentals about fluorescence and fluorescent dyes are introduced, followed by fluorescence microscopy and principle of laser confocal fluorescence microscopy (LCFM). Sample preparation, resolution of LCFM, selection of objective lenses and case studies are covered.

2

Contact Angle in Surface Analysis

2.1 Introduction

The ability of a liquid to wet a solid surface depends on the surface energies of the solid–vapor interface, the liquid–vapor interface, and the solid–liquid interface. The surface energy across an interface is a measure of the energy required to form a unit area of new surface at the interface. The intermolecular bonds or cohesive forces between the molecules of a liquid cause surface tension. There is usually an attraction between the liquid and another substance when they are brought into contact, but the adhesive forces between the liquid and the second substance will compete against the cohesive forces of the liquid. Liquids with weak cohesive bonds and a strong attraction to the other material will tend to spread over the material. Liquids with strong cohesive bonds and weaker adhesive forces will tend to bead up and form a droplet when in contact with another material.

The definition of surface energy is the work required to increase the surface area of a substance by unit area. Surface energy derives from the unsatisfied bonding potential of molecules at a surface, giving rise to "free energy." This is unlike the molecules within a material, which have lower energy because they are interacting with like molecules in all directions. Molecules at the surface will try to reduce this free energy by interacting with molecules in an adjacent phase. The free energy per unit area is termed the surface energy for solids, and the surface tension in liquids when one of the bulk phases is a gas. On the other hand, when both phases are condensed (i.e., solid–solid, solid–liquid, and immiscible liquid–liquid interfaces), the free energy per unit area of the interface is called the "interfacial energy."

The term surface energy is also related to surface hydrophobicity. Whereas surface energy describes interactions with a range of materials, surface hydrophobicity describes these interactions with water only. Because water has a high capacity for bonding, a material of high surface energy (i.e., high bonding potential) can have more interactions with water and consequently will be more hydrophilic. Therefore, hydrophobicity generally decreases as surface energy increases. Hydrophilic surfaces such as glass have high surface energies, whereas hydrophobic surfaces such as polytetrafluoroethylene (PTFE) or polystyrene have low surface energies.

The determination of solid–vapor (γ_{sv}) and solid–liquid (γ_{sl}) interfacial tensions is important in a wide range of problems in pure and applied sciences. Due to the immense difficulties encountered in the direct measurement of surface tension when a solid phase is involved, indirect approaches are usually called for. Several approaches have been used to estimate solid surface tensions: direct force measurements [1–9], contact angles [10–17], capillary penetration into columns of particle powder [18–21], sedimentation of particles [22–25], solidification front interaction with particles [26–33], film flotation [34–38], gradient theory [39–42], Lifshitz theory of van der Waals forces [42–45], and theory of molecular interactions [46–49]. Among these methods, contact angle measurements are believed to be the simplest.

Contact angle can be measured by establishing the tangent (angle) of a liquid drop with a solid surface at the base. The possibility of estimating solid surface energies from contact angles relies on a relation that has been recognized by Young [50]. The contact angle of a liquid drop on a solid surface is defined by the equilibrium of the drop under the action of three interfacial tensions (Figure 2.1): solid–vapor, γ_{sv}; solid–liquid, γ_{sl}; and liquid–vapor, γ_{lv}. This equilibrium relation is known as Young's equation:

$$\gamma_{lv} \cos \theta_Y = \gamma_{sv} - \gamma_{sl} \tag{2.1}$$

where θ_Y is the Young contact angle, that is, the measured contact angle.

Young's equation contains only two measurable quantities: the contact angle θ_Y and the liquid-vapor surface tension γ_{lv}. To determine γ_{sv} and γ_{sl}, an additional relation relating these quantities must be sought.

Because γ_{lv}, γ_{sv}, and γ_{sl} are the thermodynamic properties of the liquid and solid, there should be a single, unique contact angle. However, contact angle phenomena are not as straightforward [51–53]. In particular, the contact angle made by an advancing liquid (θ_a) and that made by a receding liquid (θ_r) are not identical; nearly all solid surfaces exhibit contact angle hysteresis, H (the difference between θ_a and θ_r):

$$H = \theta_a - \theta_r \tag{2.2}$$

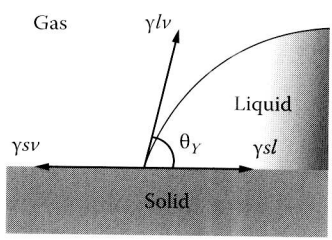

FIGURE 2.1
A contact angle of a liquid sample.