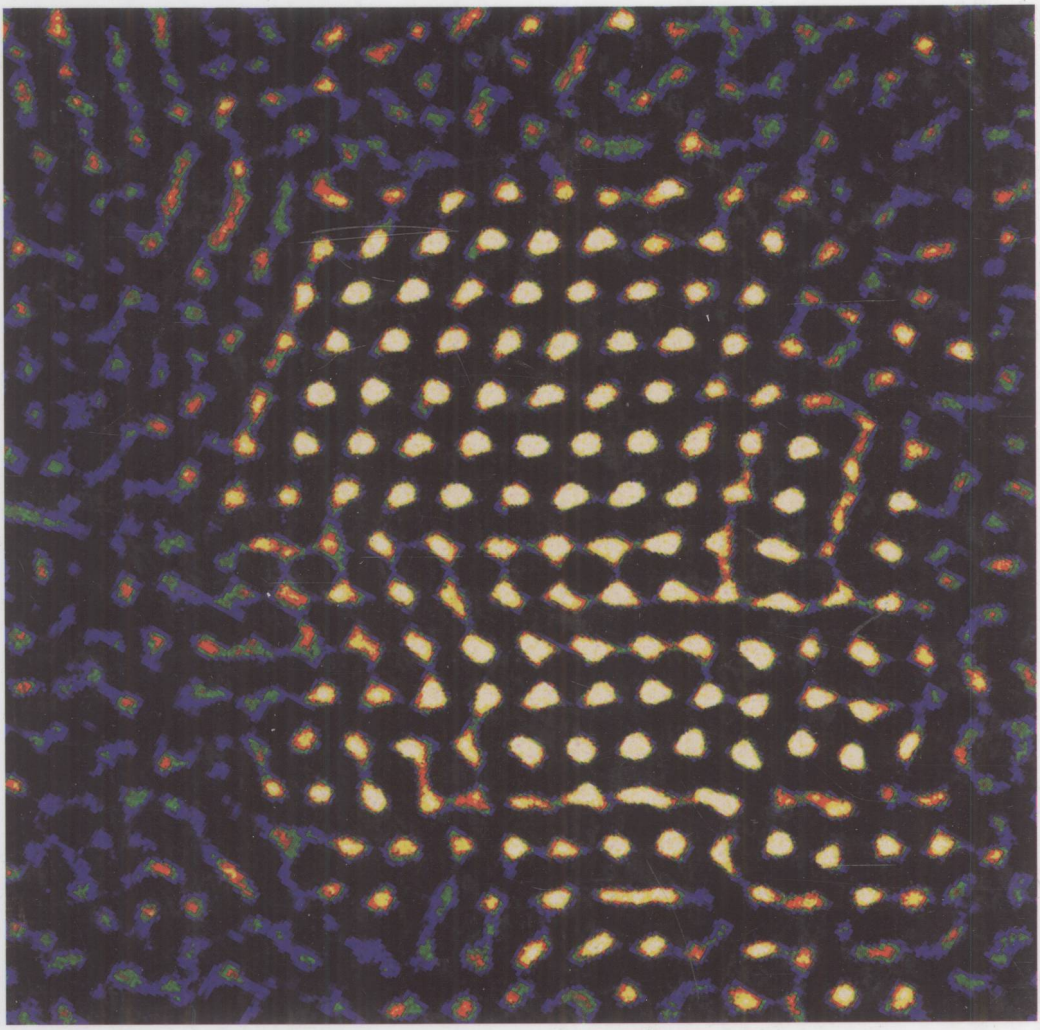
RSC Nanoscience & Nanotechnology

Edited by Angus I Kirkland and John L Hutchison

Nanocharacterisation



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Preface

In presenting these chapters with the common theme "Nanocharacterisation", it is instructive to note the explosive development of nanotechnology over the past few years. Although the term itself is relatively recent, its origins can be traced back to the late 19th century, with the development of colloidal science. The medieval craftsmen who produced the stained glass that adorns many of Europe's great cathedrals unwittingly used nanotechnology: their addition of gold chloride to molten glass produced tiny, uniformly sized gold spheres ($\sim$50 nm in diameter) that impart the deep ruby-red colouration that is a characteristic feature of many famous windows; similarly, silver nanocrystals produced an intense yellow colouration.

The use of nanoscale particles with high surface areas has also been exploited for many years in industrial catalysis, and again the preparation of these materials has used "nanotechnology" in various forms.

The anticipation of many of the potential benefits of nanotechnology may be traced back to a lecture "*There's Plenty of Room at the Bottom*" delivered by Richard Feynman to a meeting of the American Physical Society in 1959. Describing a process by which the ability to manipulate individual atoms and molecules might be developed, Feynman conjectured:

"*What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can't see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do*".

In the course of his lecture, Feynman also noted that scaling issues would arise from changes in the magnitude of various physical phenomena and suggested that electron microscopy would play a key role in the characterisation of these materials.

The term "nanotechnology" was coined and defined in the mid-1970s in a paper presented by Norio Taniguchi (N. Taniguchi, "On the Basic Concept of 'Nano-Technology'," *Proc. Intl. Conf. Prod. Eng. Tokyo*, Part II, 1974, Japan Society of Precision Engineering) in which it was suggested that it "*consists of*

the processing of, separation, consolidation, and deformation of materials by one atom or one molecule."

Subsequently, this basic definition was explored in greater depth by Eric Drexler, who vigourously promoted the technological significance of nanoscale phenomena and devices. ["*Engines of Creation: The Coming Era of Nanotechnology and Nanosystems: Molecular Machinery, Manufacturing, and Computation*", (ISBN 0-471-57518-6).]

At the time of writing "nanotechnology" embraces a large (and growing number) of techniques that are used to create and characterise structures on a size scale below $\sim$100 nm. Included in these are methods used for the fabrication of nanowires, lithographic techniques routinely used in semiconductor fabrication, focused ion beam (FIB) machining and related techniques used for the production of micro-electro-mechanical systems (MEMS) and molecular self-assembly.

In the early 1980s two significant developments had a major impact on characterisation aspects of nanotechnology: the invention of the scanning tunneling microscope and the synthesis of small carbon clusters. The development of this instrument in 1981, for which Gerd Binning and Heinrich Rohrer were awarded the Nobel Prize in 1986, followed on exactly 50 years after the development of the first transmission electron microscope in 1931 by Max Knoll and Ernst Ruska, the latter sharing (somewhat belatedly) the same Nobel Prize. This has in turn spawned a plethora of other scanned probe microscopy techniques including atomic force microscopy, magnetic force microscopy, electrostatic force microscopy and others.

The discovery in 1985 of single, closed-shell carbon nanostructures (e.g. C_{60}) known collectively as fullerenes, by Harold Kroto and his colleagues, for which they also were awarded the Nobel Prize in 1996, and the recognition of carbon nanotubes, provided much of the impetus for what would become an unprecedented and explosive worldwide development and interest in nanostructures.

These developments have driven a need for ever-more powerful techniques for structural and chemical characterisation on the "nanoscale" and "nanocharacterisation" – the theme of this book, now encompasses a diverse range of techniques that are the essential tools underpinning much of nanotechnology.

In attempting to give an overview of the different techniques now in regular use in nanocharacterisation we have been necessarily selective and we note that other microscopies are still developing that will certainly find a place in the armoury with which nanotechnologists will pursue their quest for ever-smaller and tighter-controlled structures.

In the chapter devoted to high-resolution (transmission) electron microscopy David Smith illustrates how this technique has evolved into a widely used tool in modern nanostructure research, highlighting the problems relating to interpretation of image contrast, as well as providing numerous examples showing how HRTEM has been used to provide unique insights into local microstructure of nanocrystalline materials.

The development of the scanning transmission electron microscope in the 1970s by Albert Crewe and colleagues produced instruments that could use the

signals generated by scanning an electron beam across a thin specimen in a controlled manner. The chapter by Andrew Lupini, Stephen Pennycook and their coworkers outlines this technique and demonstrates how the recent application of aberration-correcting devices in STEM instrumentation is now capable of producing sub-Angstrom imaging and spectroscopy of nanostructures.

Complementing the above are the various scanned probe microscopy techniques that have emerged following the initial development of the scanning tunneling microscope. These instruments rely on a variety of surface/probe interactions and delicate rastering mechanisms to obtain images with extreme depth sensitivity to various parameters thus revealing many physical and electronic properties with atomic resolution. The additional ability to interact with *individual* atoms on surfaces in a precisely controlled manner also opens up an exciting range of opportunities for nanoscale manipulation and fabrication. Martin Castell in his chapter provides an overview of this field, and explores in detail the use of these techniques in nanoscience.

In addition to structural information, local chemical composition, bonding and electronic states are key aspects of nanostructures. A range of spectroscopic techniques is now available for probing local structures on the atomic scale. Among these, electron energy-loss spectroscopy and energy dispersive X-ray analysis have emerged as the most powerful and widely used. These techniques probe, respectively, the energy loss of electrons passing through a thin specimen and the X-rays generated by the incident electron beam. The chapter by Rik Brydson provides an overview of the physical principles involved in these and demonstrates how they are now being used to probe local chemistry and bonding at the atomic level.

In many applications of nanotechnology the measurement of the magnetic and electrical properties of individual nanoscale objects is becoming increasingly important. Relatively recent instrumental developments have enabled the technique of electron holography, first proposed by Gabor in 1947, to be used, to obtain measurement of these. Rafal Dunin-Borkowski and coworkers describe the theory and practice of this technique and its application to a range of important nanostructured magnetic and electronic materials.

As nanostructures become smaller, their 3-dimensional shape assumes much greater importance. This is particularly the case for supported catalysts, where active sites may be determined by such entities. Although electron tomography had been previously applied successfully to biological structures it has only recently been extended to for applications in nanoscience. Paul Midgley and Mathew Weyland survey the instrumental, theoretical and computational requirements of this important technique and illustrate how it can be used to gain 3-dimensional information from a wide range of technologically important materials.

The ability to carry out or induce chemical reactions on a very small scale is also crucial to many aspects of nanotechnology and the ability to observe these *in situ* is a particularly powerful combination. This can be achieved with specially modified instrumentation that allows a controlled, gaseous environment around the specimen. In the concluding chapter, Pratibha Gai gives an

account of the design and use of an environmental transmission electron microscopy facility including a description of the physical principles involved in its design together with numerous case histories describing some of the insights gained into some important chemical processes.

In summary, our aim in preparing this book has been to gather together a selection of articles written by internationally recognised experts that describe some of the characterisation techniques that are currently used in studies of nanostructured materials.

We hope that the handbook will provide a valuable resource to all involved in the characterisation of nanomaterials.

Contents

CHAPTER 1

Characterisation of Nanomaterials Using Transmission Electron Microscopy

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1.1 Introduction

The Transmission Electron Microscope (TEM) has evolved over many years into a highly sophisticated instrument that has found widespread application across the scientific disciplines. Because the TEM has an unparalleled ability to provide structural *and* chemical information over a range of length scales down to the level of atomic dimensions, it has developed into an indispensable tool for scientists who are interested in understanding the properties of nanostructured materials and in manipulating their behaviour.

The resolution of the optical microscope is restricted by the wavelength of visible light, which thus precludes atomic-scale imaging. In contrast, an energetic electron has a wavelength of much less than 1 Å (where 1 Å $= 10^{-10}$ m), so that an enormous improvement in resolution can be achieved, at least in principle, by using a beam of fast electrons for imaging. A suitable combination of (magnetic) electron lenses is required, both for focusing the electron beam onto the object and also for providing an enlarged image. Maximum magnifications at the microscope are typically close to or exceed one million times, so that details of the nanoscale object are clearly visible on the final viewing screen or recording medium.

Image formation in the TEM is more complicated in practice than is the case for the optical microscope. Strong magnetic fields are needed for focusing the electron beam, and these cause electrons to take a spiral trajectory through the lens field. In addition, a major restriction on ultimate microscope performance

results from unavoidable aberrations of round electron lenses. Primarily, due to the need for a compromise between small-angle diffraction effects and wide-angle spherical-aberration limits, the resolution, d can be roughly expressed by an equation of the form

$$d = A\, C_s^{1/4}\, \lambda^{3/4} \tag{1.1}$$

where C_S is the spherical aberration coefficient of the objective lens, λ is the electron wavelength, and A is a constant with a value ranging from 0.43 to 0.7 depending on the type of imaging (coherent, incoherent, or phase contrast). Values of d typically range from about 3.0 Å down to 1.0 Å as electron energies are increased from 100 to 1250 keV. Modern-day TEMs operating at 200 or 300 keV have resolution limits well below 2.0 Å, which is comparable to the spacing between atoms. Individual columns of atoms can thus be resolved in crystalline materials, which must first, however, be oriented so that the incident electron beam is aligned along some major crystallographic zone axis of the sample.

The power of the technique is illustrated by the example in Figure 1.1, which shows the boundary region between two Al crystals, both of which are oriented so that the electron beam is parallel with the [001]-type zone axis. Each black spot in the image marks the position of a column of Al metal atoms viewed in an end-on geometry. It is obviously straightforward to visualise the periodic array of misfit dislocations (arrowed) that accommodate the angular misfit of 6° between the two crystals, and further analysis would enable the detailed atomic structure around the dislocation core to be determined.

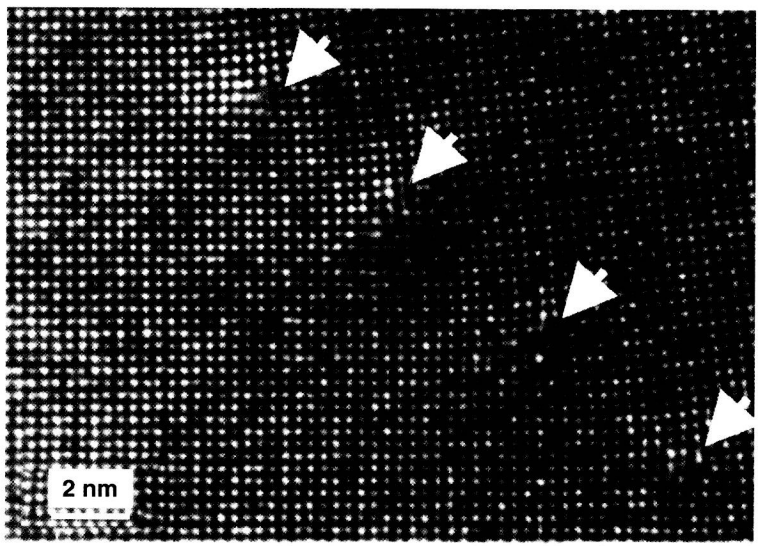

Figure 1.1 Atomic-resolution electron micrograph of Al 6° [001] symmetric tilt grain boundary with misfit accommodation by [110]/2 edge dislocations (arrowed). Each black spot corresponds to projection of an individual Al atomic column.

This chapter begins by providing a brief introduction to the TEM and some of the key aspects of high-resolution imaging. Applications to nanostructured materials are then described in greater detail, and some emerging trends and unresolved issues are briefly discussed. For further information about microscope operation and more details about applications to a broader range of materials, the interested reader is referred to the review articles and monographs listed at the end of the chapter.[1–9]

1.2 Imaging

1.2.1 Transmission Electron Microscopy

In the standard TEM operating mode, which is commonly referred to as amplitude or diffraction contrast imaging, only a fraction of those electrons that have passed through the sample are used to form the highly magnified final image. Most of the scattered (or diffracted) electrons are prevented from reaching the image plane by positioning a small objective aperture located in the back focal plane of the objective lens. This aperture thus serves to determine the image contrast. For the case of crystalline samples, the electron diffraction pattern (EDP) is used to ensure that the orientation of the specimen relative to the direction of the incident electron beam will satisfy a strongly diffracting condition. Many common structural defects have a highly characteristic appearance under such diffraction contrast conditions. The spacings and angles between crystal lattice planes can also be determined if the EDP is first calibrated using a known material. In addition, the availability of a crystalline substrate or support can provide a convenient method for sample orientation during observation. By using the substrate EDP for reference purposes, internal interfaces can be aligned perpendicular to the electron-beam direction so that any changes in the microstructure of thin films and multilayers can then be determined as a function of film thickness. As an example, Figure 1.2 shows a multilayered Magnetic Tunneling Transistor (MTT) deposited directly on the native oxide of a Si substrate.[10] The individual layers of the MTT can be clearly recognised, and their thickness uniformity is easily confirmed. Finally, it should be appreciated by the reader that examination of such complex samples with the TEM can represent a serious challenge to the electron microscopist. Because of considerable differences in thinning rates, it will often be difficult to prepare samples that are electron transparent across the entire region of interest simultaneously. Descriptions of different approaches for preparing electron-transparent specimens can be found elsewhere.[11,12]

1.2.2 High-Resolution Electron Microscopy

In the technique of High-Resolution Electron Microscopy (HREM), a much larger objective aperture (or sometimes none at all) is used. The directly transmitted beam can then interfere with one or more diffracted beams, and

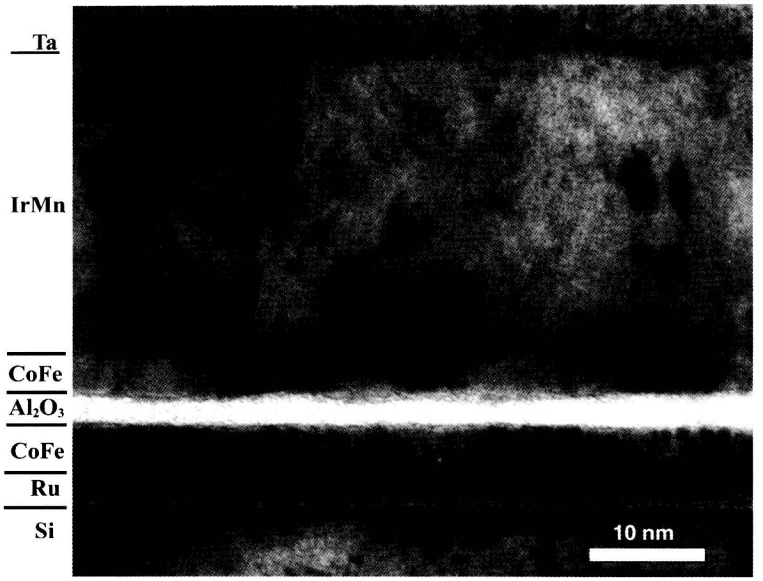

Figure 1.2 Bright-field electron micrograph showing the cross section of a typical MTT device structure with a Ru seed layer between the Si(001) collector substrate and the CoFe base layer. Reproduced from Ref. 10.

the contrast across the image will depend on the relative phases of the various beams. This imaging mode is thus often referred to as phase contrast imaging. When the microscope imaging conditions are properly adjusted (lens defocus, image astigmatism, incident beam alignment) it is possible to interpret phase-contrast images in terms of the projected crystal potential provided that the specimen thickness is not too great (less than 10 nm preferred). Indeed, individual atomic columns can be separately resolved in many crystalline inorganic materials using the latest generations of HREM instruments.[1] High electron doses, typically $\sim$500–2000 electrons per square Å, are required to record such images, which means that specimens intended for high-resolution studies must be relatively resistant to electron-irradiation effects. It is impossible to examine most organic materials and polymers directly under such intense imaging conditions. By using a specimen-heating holder, and by adding a TV rate image pickup system to the base of the electron microscope lens column, dynamic events can be followed in real time without significant loss of spatial resolution.[13,14]

Over the past 40 years, HREM has been used to characterise a wide range of inorganic materials. Important applications include determining the microstructure of crystalline defects, interfaces and grain boundaries, investigating nanocrystalline features in amorphous films, and studying small particles in heterogeneous catalysts. The characterisation of magnetic thin films and multilayers, for example, continues to be very important, since layer continuity and defect microstructure are crucial to the viability of recording media. High