1. Introduction: Structure and Structuring of Solids

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1.1 Scope

This volume combines several articles concerning novel techniques, in which X-ray optical methods are utilized for the analysis and processing of solid-state materials. X-ray techniques have consistently been vital tools for the understanding of crystalline solids and their ideal as well as real atomic arrangements [1.1, 2]. The necessary restriction for this volume led to a selection of new techniques which presently appear particularly promising for playing a significant role in the future development of advanced mastering of solids, such as in the microelectronics of large-scale integration. Modern X-ray methods lead to increased understanding of the crystal structure as well as to highly resolved compositional and geometrical structuring of solids [1.3].

Emphasis is therefore first placed on refined techniques in which X-ray optics can reveal lattice defects in single crystals of high perfection. Here, silicon and quartz are the typical prototype materials. Demonstration of new X-ray methods for fine structure analysis of well-defined isolated imperfections has emerged in parallel with the cultivation of large, highly controlled single crystals. The two contributions on X-ray topography in this volume deal with this aspect. X-ray interferometry, another topic of this book, is a new experimental method in which strong mutual interaction with material science exists also. The demonstration of the feasibility of X-ray interferometers led to extension into the neutron regime, but also enabled some basic experiments in the physics of elementary particles to be performed.

Optical technology in the visible spectral regime has played a significant part in the rise of new generations of microelectronic devices, especially in the field of semiconductor circuits of ever-increasing number and density of functions. The wavelength of the commonly employed ultraviolet spectral range now limits further substantial increases in density and complexity [1.4]. Shorter wavelengths can be provided for enhanced spatial definition by either electron beams or by X-rays. One chapter of this book therefore deals with the rapidly developing field of X-ray lithography.

Sources of X-rays have been worrisome because of the notoriously low conversion efficiency of electrical input power into X-ray photons [1.5]. This feature had limiting effects on the ease and applicability of X-ray methods. The first chapter of this book therefore deals with the strongest conventional sources which are available today: rotary anode generators. Most of the methods described later presently rely on such generators.

Another type of source is currently becoming available; it promises to lead to many important results. This source is "synchrotron radiation", originating from accelerated electrons in synchrotrons or storage rings [1.6]. This very efficient contemporary development is not covered by a chapter here since an entire volume of the series "Topics in Applied Physics" is planned for the near future.

Missing in this volume are many other subjects falling into the category of X-ray techniques related to solid-state science and technology. Space restriction forces us to merely list some of them here and stimulate interest by quoting a few references, obviously without any claim of completeness. The entire field of crystal structure determination [1.1, 7], especially with the new developments in computer-automated data processing [1.8], is not represented in this volume. Diffuse scattering analysis [1.9] and X-ray Raman scattering [1.10] could not be covered here. Fluorescent analysis [1.11], stress analysis [1.12], and the vast, rapidly expanding field of X-ray photoelectron spectroscopy (ESCA) [1.3] cannot be touched upon here. There exists a great deal of literature on these topics; some fields of particular significance are currently under consideration for the present series "Topics in Applied Physics". Soft X-ray spectroscopy, for example using grating spectrometers, is adequately described elsewhere [1.14]; X-ray microscopy has seen a number of new developments since the publication of the book by *Cosslett* and *Nixon* [1.15]. The need for imaging of X-ray emitting objects for a subsequent spatial or spectral analysis has been particularly important for plasmas, such as in astrophysics or for fusion research [1.16].

1.2 X-Rays and Solids

1.2.1 Optics and Solids

The remarkable renaissance of optics during the last two decades was in part due to progress in solid-state materials and devices. The most noteworthy examples are the ruby laser, semiconductor injection lasers, light-emitting diodes, and the great variety of solid-state radiation detectors as well as the low-loss fiber optical waveguide materials. Controlled and efficient mutual conversion between electromagnetic radiation and electronic processes in the solid is now feasible in the visible and infrared regimes. The injection laser [1.17] demonstrates that compositional control within fractions of a micron inside a semiconductor is a prerequisite to obtain a source for coherent radiation in the wavelength range of about one micron. Comparable accuracies and utilizations in the ultraviolet range and beyond are, however, still seriously impeded by the stringent conditions for control of very small dimensions and the onset of high absorption. Solid-state technology has begun to change optics markedly: traditional freespace propagation with utilization of individual optical components is gradually being replaced by a technique of producing, guiding, modulating, and converting electromagnetic radiation within highly structured solids, the aim of this development being a truly "integrated optics" [1.18].

1.2.2 X-Rays and Solid-State Physics

Solids have played a decisive role in the history of X-ray physics and technology. Experimental proof of the wave nature of X-rays was achieved in the classical fashion by diffraction at slits; however, of revolutionary character was the diffraction experiment using the three-dimensional grating of a regular single-crystal solid. This experiment by *Laue* and his collaborators [1.19] immediately opened up the field of diffraction analysis for solids, thus marking the beginning of solid-state physics with the experimental proof of the essential periodicity of a solid and the precise determination of interatomic distances. A direct result was the early description of a solid within reciprocal space, a concept which later became an essential foundation of all solid-state theory. Later developments focused on the real structure of solids, in particular the extremely strong influence of specific lattice defects, which could be positively identified and quantified only by X-ray or electron diffraction techniques.

The understanding of wave fields within a solid of lattice constant about equal to the wavelength was achieved through the dynamical theory [1.20] and the interpretation of such unusual phenomena as the anomalous transmission [1.21]. Crystallography and wave mechanics had to be combined when the characteristic dimensions, lattice parameter and wavelength, become of equal magnitude.

1.2.3 Outlook

The intricate and complex effects resulting from this interaction between an electromagnetic wave field and a regular atomic array still represent a fruitful area of research, development, and applications. It is my feeling that we can presently expect a time of renewed achievements in this field. I base this hope on the vigorous efforts and remarkable success already apparent in the control of the composition of solids. One particularly striking example has been given through the techniques of molecular-beam epitaxial crystal growth [1.22]: it now appears feasible to control individual layers of a mixed-crystal semiconductor material [1.23]. The techniques of proving and analyzing this remarkable claim of material control down to atomic dimensions must obviously be based on diffraction techniques. On the other hand, it now seems realistic to anticipate that solid structures of such finely tuned character with designed lattice parameter variations or having prescribed atomic species within specified lattice planes cannot fail to make their impact in confining, guiding, or modulating wave fields in the X-regime to heretofore unknown precision. New effects and applications will thus emerge from these — admittedly difficult and painstaking — experiments in designing solids. It is the purpose of this volume to contribute towards progress in this interdisciplinary task by combining solid-state aspects with X-ray technology.

1.3 Sources

The standard arrangement of any optical experiment consists of the sequence: source, propagation medium, specimen, detector. For each spectral region usually one of these components clearly limits experimental efficiency and accuracy. For example, in the infrared, the detector problem presents particular difficulties due to the small quantum energy of those photons. In the X-ray regime, however, the photons are sufficiently energetic to utilize a wide range of reactions and effects for detection, although noise may present problems. (A discussion of the detector aspect will be included in Chap. 6, since live topography cannot be satisfied with integration in a photographic plate but is forced to find an efficient down-conversion process into visible photons.) The source is therefore the central experimental problem.

X-ray sources typically have conversion efficiencies of only fractions of a percent and are beset by the task of rapid removal of the excess heat which would otherwise damage the active anode region. Today's very widely used sources are therefore of the rotary anode type. A great deal of development work has gone into these generators. Chapter 2 of this book, by *Yoshimatsu* and *Kozaki*, is a detailed description of the history, the present state of the art, and the anticipated trends in this technology.

X-ray lasers are today the subject of much discussion and speculation [1.24]. There is currently a great deal of activity in producing and verifying a coherent emission, usually in the region of very soft X-rays having wavelengths of several hundreds of Angstroms. We felt that this field had not yet sufficiently matured at the time of writing this book to warrant inclusion of this topic. It is, however, quite obvious that any breakthrough in obtaining a laser-like source for X-rays would greatly influence and stimulate many applications, including those covered by the chapters of this volume [1.27].

1.4 Structuring with X-Ray Techniques

Spiller and *Feder* cover a topic of great current interest in Chapter 3 of this volume. X-ray lithography for solid-state device applications is being considered as a feasible way to greatly enhance the degree of geometry control which is an absolute necessity for increasing the density of integrated circuit functions and reducing the size of their individual elements. The idea of using wavelengths shorter than the usual visible light to improve microscope resolution is, of course, an obvious one and has been treated in great detail for quite some time [1.15]. It appears, however, that the definite industrial need for finer structuring and the associated great effort in this field will lead to renewal of interest in this general field of X-ray microscopy with far-reaching applications in many other fields, including, of course, biology and medicine. An example of this is the work by *Spiller* et al. [1.25], in which they used the subsequent inspection of their lithographic image by means of a highly magnifying scanning electron microscope to achieve extremely high resolution. The future will show whether the further development of such combined techniques might eventually lead to an optimal microscopy, to be applied to biological macromolecules.

The lithographic activity of the impinging X-rays results from the liberation of photoelectrons in a suitable resist, which then leads to sharply localized development of this photosensitive resist with ensuing usable changes in chemical features, such as solubility or etching rates. The question arises why there is need to first convert high-energy electrons into X-ray radiation if it is the reconverted electrons that cause the essential effect. Indeed, development of electron beam lithography is currently receiving greater emphasis than is X-ray lithography for solid-state device applications. One can often hear the opinion today that the rapidly progressing technology of electron beam lithography may render X-ray techniques uninteresting. There are, however, advantages for X-ray methods. The conversion to electromagnetic radiation facilitates propagation, especially through interfaces such as windows. The reduced sensitivity to external fields favors waves over charged particles. Electron scattering and charging effects are avoided. There is less sensitivity to dust and contamination in the exposure process. The essential problem of aligning the specimen for multiple consecutive exposures requires attention for X-ray systems, especially using synchrotron radiation. All these options are, however, as yet not thoroughly determined and will be strongly influenced by considerations of economy.

1.5 Interferometry

Optics in the X-ray regime is characterized by a lack of dispersive effects, on which elements such as lenses or prisma are based in other spectral regions. The external frequencies greatly exceed the frequencies of the polarization oscillators. One can therefore approximate the index of refraction in the X-ray region by

$$n = 1 - C\varrho\lambda^2 \tag{1.1}$$

where ϱ is the density of the material and λ the wavelength. The constant C is of the order of 10^{11} m kg^{-1}. This equation shows the independence of specific material properties. We further see that the index n is always slightly smaller than unity. For a density of $10\,\mathrm{g\,cm^{-3}}$, one has at 1 Å merely a deviation of about 10^{-5} from unity. Utilization of this small difference of the index of refraction versus vacuum would lead to impractically long focal lengths.

Bragg reflection from regularly spaced atomic planes of a solid can fortunately be utilized for optical components. A very sophisticated type of interferometry, using highly perfect single crystals, has recently arisen. *Bonse*, one of the original researchers in this new field, and *Graeff* describe the principles and applications of these methods in Chapter 4. X-ray radiation is so similar here to neutrons of comparable wavelengths that these two types of undular excitation have been combined. Neutron interferometry has permitted a very beautiful experiment of elementary nature, in which the phase shift caused by gravitational interaction could be determined; this experiment is the only one where the constant h of quantum theory appears together with the elementary constant of gravitation.

X-ray interferometry has been applied to optical comparison of materials against a standard of the same material. The extreme conditions of geometry control require that the individual components of the interferometer must often be machined out of one perfect crystal with long crystallographic coherence. This requirement has thus far somewhat restricted a more general usage of X-ray interferometry for, say, silicon materials characterization. Hopefully, further progress will occur, leading to a novel, highly sensitive probe for crystalline structure which ought to be useful for the undoubtedly yet-increasing standards of crystalline perfection for future solid-state materials.

1.6 Defect Structure Topography

Deviations in the regular crystallographic arrangement are caused by lattice defects, such as dislocations, stacking faults, and internal boundaries. These defects may cause uncontrolled alterations in many physical parameters and thus present undesirable properties of the material. Diffraction techniques are well suited for the detailed analysis of such defects; X-ray diffraction is specifically advantageous since it is a nondestructive technique not requiring special sample preparation. The crystal may be viewed in the reflected light of one particular Laue reflex. The information concerning the crystalline perfection is contained in the intensity variations of this reflex. A complete image of the defect structure for a large sample can then be obtained by systematic scanning of the specimen and provision of a definite correlation between sample and detector, for example by rigidly connecting them and moving the entire arrangement with respect to the incoming X-ray beam. This technique, called topography, is of great practical importance today for the characterization of materials as well as for investigating the influence of processing on crystal structure [1.26].

This volume does not concern itself with a general review of topography, but describes two specific trends of topography in more detail. *Authier* treats in Chapter 5 the technique of section topography. This method yields detailed information on the nature of defects in nearly perfect crystals and enables one to make specific statements concerning the depth distribution of defects in comparatively thick samples. The predominantly theoretical nature of *Authier*'s contribution indicates the great amount of mathematical treatment necessary for extracting structural information from these disturbances of the wave fields within the crystal.

Topography today uses mostly photographic emulsions for mapping the image of a specimen. This restriction is caused by the comparatively weak sources, calling for integration of the X-ray flux by the photographic plate. A nonmagnifying technique results, which in turn places high requirements on the quality and grain size of the plate in order to retain detailed information. In situ measurements of dynamic effects are impossible. Topography has thus resisted the general trend of replacing analog detection methods with principles of digital counting. Coupling to modern signal processing methods is absent here, which represents a definite weakness of the method. It is therefore understandable that considerable efforts have been applied to finding a direct viewing technique, which is usually called "live topography". A set of digital signals which can be further processed by using the readily available techniques of television electronics and digital data handling leads to the goal of all of these techniques—a final television image. *Hartmann* summarizes in Chapter 6 the present state of this development which promises not only to furnish more detailed information for the technology of materials processing but also gives hope for a better basic understanding of defect dynamics.

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