Reading and Writing with Electron Beams

Reaching to smaller and smaller scales, modern electron beams are used for studying atomic arrangements inside solids and for imprinting tiny patterns on semiconductor chips.

J. Murray Gibson

Cathode rays, accelerated by tens of thousands of volts or more, have had immense scientific and technological value in the hundred years since Joseph John Thomson used them to discover the electron. The most familiar use of these electron beams is in cathode-ray tubes—as used in television sets and computer displays, for example. Electron microscopy, a less familiar use, has been a keystone method for visualizing the structure of materials on the atomic level, and continues to offer exciting developments. Electron beams have also found an important role in patterning semiconductor chips, and they may even supplant optical beams as a basis for lithography in the 21st century. Before the discovery of electrons, photons dominated microscopy. Now it seems that in both microscopy and lithography, electrons will take over. More power to rest mass! In this article, I give a glimpse of the state of the art in electron microscopy and lithography, and point out where I believe these fields are going.

The 1986 Nobel Prize in Physics was awarded to three pioneers of electron microscopy: Ernst Ruska, for his invention—over 50 years earlier—of the transmission electron microscope, and Gerd Binnig and Heinrich Rohrer for their invention of the scanning tunneling microscope—a powerful electron-based tool (but not covered in this article). In their Nobel citation, Binnig and Rohrer were rightly given credit for the impact of their invention on solid-state and surface physics. Strangely, though, Ruska's Nobel citation left out the extensive applications of transmission electron microscopy in solid-state and materials physics. Rather, it mentioned only the valuable biological applications—that is not a fair reflection of the relative contributions of these valuable and complementary techniques to solid-state and materials physics.

This situation resonates with my experience that solid-state physicists are often unfamiliar with the basic capabilities of transmission electron microscopy, despite its widespread use in revealing materials' microstructure. Diffraction is, of course, well known to physicists. After all, many of solid-state physics' great successes have come from examining things in reciprocal space. With lenses, which are readily available for electrons, both real space and reciprocal (diffraction) space are accessible to electron beams. And filtering is possible in either domain.

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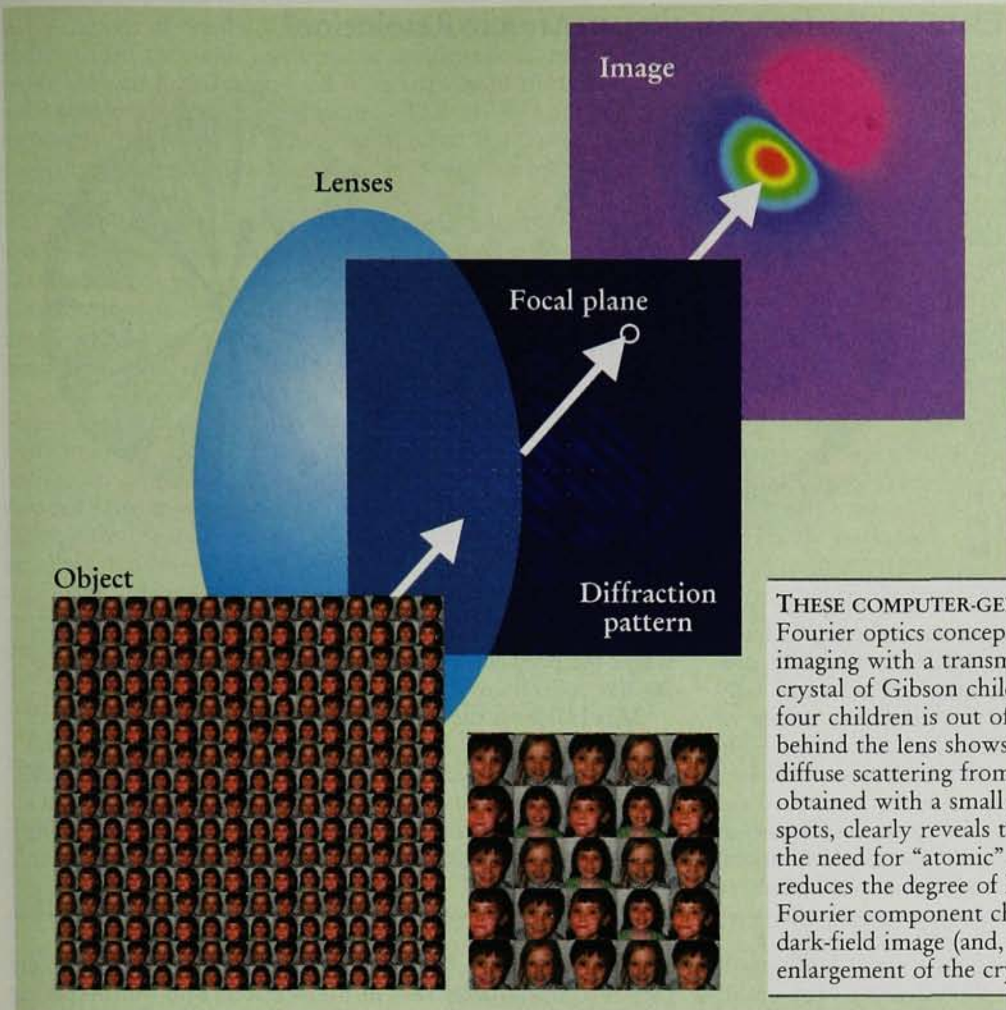
Fourier optics and electron microscopes

A simple lens is an analog device for Fourier transformation, as originally noted by Ernst Abbe in his landmark 19th-century theory for the resolution limit of optical microscopes. The Fraunhofer diffraction pattern of an object that would be formed at infinity is brought into focus in the back focal plane of a lens. This diffraction pattern is in fact the Fourier transform of the wavefront emerging from the specimen. For a crystal, with parallel electron illumination of wavelength less than the atomic spacing, a segment of the reciprocal lattice is imaged in the back focal plane. A second Fourier transform takes place as the wave propagates to the image plane, although the real space coordinate system is scaled due to magnification. Any aperture placed in the focal plane thus has the effect of Fourier-filtering reciprocal space.

To illustrate this principle more graphically, I have used an artificial imperfect crystal—a photograph of my four children, Helen, John, Margaret and Hannah—as shown in the figure on page 57. Can you spot the defect in this artificial crystal of Gibsons?

It is well known, from Abbe's theory, that a circular aperture of radius k_{ap} has the simple effect of limiting the smallest resolvable distance in the image δ to $0.61/k_{ap}$. This "objective" aperture endows transmission electron microscopy with incredible power. To resolve the lattice directly, the aperture radius must exceed the magnitude of the reciprocal lattice vector $\mathbf{g}$ of the appropriate lattice planes. Accordingly, the unscattered beam and the diffracted beam must be allowed to interfere—that is, create "phase contrast"—to form a lattice image. However, if a small aperture is used and placed around a particular diffracted beam, the image formed will reveal in real space, with limited resolution, the local diffracted amplitude—an effect known as dark-field, diffraction-contrast imaging. In this way, images are formed of dislocations, faults, granular structure and other imperfections without needing direct atomic resolution.[1] (Note the use of a small aperture to reveal the position of the defect in the Gibsons' lattice in the figure.)

These experiments, which demand less from the electron phase, can be carried out on relatively thick specimens (about 0.5 μm), thereby facilitating the study of the interior microstructure of solids. The microscopes that possess this diffraction contrast ability, including the low-



THESE COMPUTER-GENERATED IMAGES demonstrate the Fourier optics concept behind diffraction contrast imaging with a transmission electron microscope. A crystal of Gibson children contains a defect: One of the four children is out of order. The diffraction pattern behind the lens shows sharp spots with some weak diffuse scattering from the defect. The dark-field image, obtained with a small aperture around one of the Bragg spots, clearly reveals the position of the defect without the need for "atomic" resolution. Since the defect reduces the degree of local order, the amplitude of the Fourier component changes locally and is revealed in the dark-field image (and, for comparison, in the adjacent enlargement of the crystal).

energy electron microscope, have an advantage over direct imaging instruments, such as the scanning tunneling microscope, which are "stuck" in real space, and for which real-space resolution is paramount.

Resolution of electron optics

Transmission electron microscopes hold the world record for optical resolution, currently at about 0.1 nm.[2] The two most severe restrictions on surpassing this limit are the spherical and chromatic aberration coefficients of the lenses.

Typically, electron optical instruments use "round" (cylindrically symmetric) magnetic lenses. Although these round lenses can have very low aberration, it is impossible to completely remove chromatic and spherical aberrations from them. This situation is a consequence of Maxwell's equations or—more simply—of the fact that all round magnetic lenses are convergent and have the same sign as these aberrations.

For an optimally designed lens, the aberration coefficients, which determine the magnitude of blurring, are of the same order of magnitude as the focal length of the lens. High magnetic fields in small volumes lead to short focal lengths, and are obtained by concentrating magnetic flux across a small gap between high-permeability "polepieces." With peak field values of a few tesla, focal lengths of around 1 mm at up to 1 MeV in electron energy can be obtained. The resolution is given by $0.7(C_s\lambda^3)^{1/4}$, where C_s is the spherical aberration coefficient and λ is the electron wavelength, permitting a value of 0.1 nm at the highest voltages.

Such high-voltage microscopes are extremely large and expensive (about $50 million each), and inflict severe damage on specimens. The few existing in the world today are in Japan or Germany. More conventional transmission microscopes operate at 200–400 kV, where damage is less but resolution is poorer—typically no finer than 0.15 nm. There are dozens of such instruments in the US today, and they each cost about $1 million. Several approaches to improving the resolution of these microscopes are being investigated.

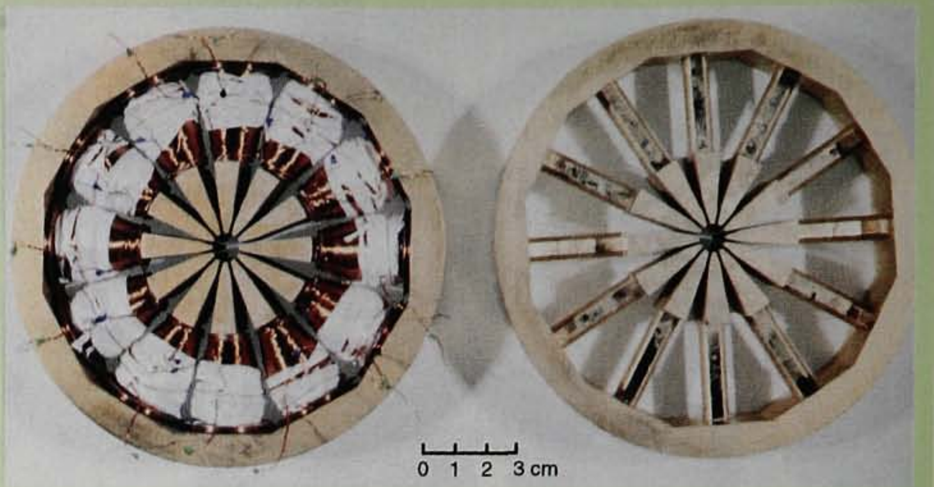
Why improve the resolution below 0.1 nm when the bonds between atoms in most materials are larger than this value? In fact, many interatomic planes in crystals have smaller spacing than 0.1 nm, and imaging these is necessary to visualize crystalline materials projected along a variety of directions. When imaging the atomic structure of a grain boundary, for example, it is almost essential to simultaneously image the two crystals on either side along a high-symmetry zone axis. The higher the resolution, the less limiting this very severe constraint is on the types of interfaces that can be studied.

Improved resolution can also circumvent a fundamental limitation of transmission microscopy: It forms images that at best are only a two-dimensional projection of a three-dimensional structure. By tilting the specimen and examining the same area in different projections, we can tomographically recreate the three-dimensional structure. Although this technique is now used at the 1 nm scale for biological specimens, its application to atomic reconstruction would require a resolution of better than 0.05 nm.

Improved electron–optical performance in microscopes has other advantages. To achieve the smallest aberration coefficients, highly excited immersion-type magnetic lenses must be used. In these, the specimen sits in the narrow gap between the magnetic polepieces, a constraint

Box 1: Electron Surface Imaging at Atomic Resolution?

The scanning electron microscope images with great depth of field, and has become the standard tool for evaluating surfaces. With a scanned probe, a wide variety of signals can be collected, permitting such applications as voltage imaging, chemical analysis by spectroscopy and acoustic imaging. This type of microscope does not yet compete in resolution with the atomic capabilities of the scanning tunneling microscope; its usefulness comes from the large samples of arbitrary shape that can be examined without tip-dependent effects. However, there is an exciting possibility that atomic level resolution could become practicable in the scanning electron microscope. The best approach is to correct the aberrations of the electron lenses using electric and magnetic multipole elements. Similar developments are occurring in transmission electron microscopy. This idea was originally proposed by Otto Scherzer, but its practical success came only after the complex alignments were achieved by means of computer control. By correcting aberration and using a high-performance lens, we may be able to achieve atomic resolution. Alternatively, aberration correction could be used to make possible longer working distances—that is, weaker lenses—at higher resolution than in present scanning electron microscopes. That could be invaluable for semiconductor inspection equipment and environmental cell experiments. The corrector also could permit better resolution at lower electron voltages, where the problems of specimen charging and electron damage are less deleterious.



Max Haider at the European Molecular Biology Laboratory in Heidelberg, Germany, is currently pioneering work in this area.[3] The photograph, kindly supplied by Haider, shows some of the multipole elements, which have already demonstrated a resolution of better than 2 nm at 1 kV, with an aim of getting better than 1 nm resolution at an electron accelerating voltage of 500 V.

arising from the need for high magnetic fields and small aberrations. The specimen must therefore be very small and have limited motion (tilt, for example) within the polepieces. Aberration correction would increase the useful working distance of high-resolution lenses because larger-gap polepieces could then be used.

In the future, spherical and chromatic aberration may be eliminated by using asymmetrical magnetic fields from magnetic multipole lenses. Aberration correction is also improving the resolution of scanning electron microscopes. (See box 1 above. In a scanning electron microscope, a tiny pencil beam is formed and scans in a raster pattern to form an image, using low-energy "reflected" secondary electrons.)

Beyond pictures

It is a well-worn adage that a picture is worth a thousand words. In microscopy, however, one also learns to the contrary that a few well-chosen words are worth a thousand pictures. I was struck by the following remark made by Gene Golovchenko of Harvard University, not long after he began working in the field of scanning tunneling microscopy: "I used to be a scientist, and I presented data with error bars on them. Now I'm a microscopist, and it's what I say that has the error bars." This dangerous state of affairs had often existed in the past, but present work suggests that it may be removed in the future.

Quantitative approaches to transmission electron microscopy have strong foundations in the quantum mechanical theory of high-energy electron diffraction. Indeed, the interactions of electrons with atoms can be modeled well by the first Born approximation, except for the very highest atomic numbers or largest scattering angles. For the high-energy electrons, multiple diffraction is well understood as weakly bound Bloch-wave states, each of which is a superposition of several plane-wave diffracted beams. This theory has been used for many years to explain contrast at dislocations and faults (planar defects) in crystals, and to measure their characteristic displacement fields.[1]

In the past, detailed quantitative measurements were hampered by the vast amounts of data in a picture and the difficulties in obtaining accurate intensity information from photographic recording. In recent years, both these problems have been overcome. Linear recording in direct digital form is now easily accessible with cooled charge-coupled device cameras originally developed for astronomy. Powerful image measuring and processing tools are also readily available on desktop workstations. We are beginning to see the fruits of this quantitative resolution. (See boxes 2, 3 and 4 on pages 59, 60 and 61, respectively.)

The philosopher Georg Hegel emphasized that quantitative changes could lead to qualitatively different outcomes—an observation that applies to electron microscopy. There is little reason to believe that transmission electron microscopy will not achieve the quantitative accuracy of x-ray and neutron diffraction in solving structures, but it will be on a much smaller scale. This increased accuracy could lead to qualitatively new applications for transmission electron microscopy—for example, quantitative elastic strain mapping at the near-atomic level.

Developments in computer control suggest that fully automatic instruments with built-in simulation and image interpretation could eventually lead to a much wider and more robust accessibility of the technique to nonexpert microscopists. A step in this direction will be Internet-based access to national facilities in an approach similar to that used by optical and radio astronomers today.

Electron paintbrushes

Electron beams, beyond observing specimens, can also undesirably change them. However, by using beam-sensitive layers of "resist," this effect is widely—and beneficially—used to make patterns in semiconductors for electronic device fabrication and in a variety of materials for mesoscopic physics experiments. The process of pattern formation is known as lithography, after the time-honored printing process in which ink is transferred to paper through a mask.

Although electron beams less than 1 nm in diameter are now readily available, the best resolution that can be obtained in a pattern is determined by the scale of the electron interaction with the resist material—around 10 nm. A simple scanning electron microscope with a pattern generator for the scan coils suffices.

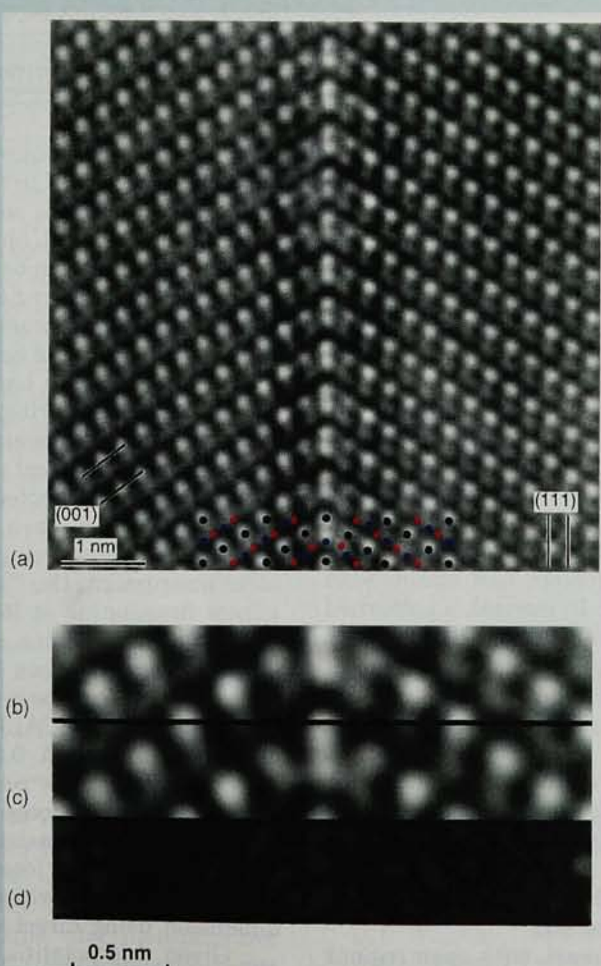
Almost all the exciting physics of mesoscopic semiconductor structures has been investigated with such instruments. Since the 1970s, the approach has been scaled up to permit the "writing" of real semiconductor devices and masks for producing wafers. For this application, the resolution is not the limiting factor, as the smallest features in today's chips have not yet reached 0.25 μm. However, since semiconductor chips require many processing steps, which must be overlaid, precise patterns must be accurately registered and aligned with previously printed features on the wafer. As a result, a modern machine for exposing semiconductors to electron beams has an interferometrically controlled stage. These machines, in so-called direct-write (that is, maskless) mode, have long been used for the development of next-generation chips, or for low-volume high-priced chips known as ASICs (application-specific integrated circuits).

High-volume moderately priced chips cannot be made by the direct-write method because the writing process takes too long. Instead, ultraviolet light is projected through masks to expose wafers coated with photoresist. These optical "steppers" can expose a single chip in a fraction of a second, and step across 40–60 wafers per hour. Current direct-write electron beam technology is limited to about 1 wafer per hour. Rather, electron beam writers are commonly used to produce the masks for optical lithography.

Even so, a revolution in lithography tools is undoubtedly coming. Due to fundamental limitations on the absorption of light as the wavelength decreases to around 100 nm, a totally new technology for printing at linewidths below 100 nm will be required. If we stick with electromagnetic radiation, we shall have to jump into the soft x-ray region, where there are daunting optical problems. Direct-write electron lithography does offer a solution, but is far too slow.

Recently, a promising electron technique has been developed at Bell Laboratories, Lucent Technologies. This technique, called SCALPEL (scattering with angular limitation projection electron lithography), embodies the advantages of electrons with a projection technique. (I

Box 2: Being Certain about Atom Positions at Interfaces



Identification of atomic structure at interfaces has been one of the important applications of high-resolution transmission electron microscopy.[2] Interfaces control mechanical strength in ceramics, electrical transport in transistors, the spread of corrosion in aircraft, tunneling currents in superconductor junctions and a myriad of other practical properties of materials. Yet, with rare exceptions, interfaces are not amenable to diffraction analysis, since they are very thin and not usually uniform.

The upper portion of the figure (a) shows an example of a phase-contrast, high-resolution transmission electron microscope image of a grain boundary in $SrTiO_3$ (courtesy of Oliver Kienzle, Frank Ernst and Mannfred Rühle of the Max Planck Institute for Metallurgy in Stuttgart, Germany). Such images, although appearing to reveal atomic positions directly, are actually the result of interference between Bloch-wave states set up in the crystal by the fast electrons and further filtered by the response function of the microscope optics. The images contain details that reflect atomic structure at the level of about 0.1 nm, but visual inspection is unreliable except at coarser resolution.

In the lower portion of the figure are given experimental data (b), together with the atomic structure assumed in the simulation (the colored dots), which can be compared with the calculated image (c). The simulation was based on quantitative refinement, and the small residual differences—of order the experimental errors—are displayed in the bottom part of the figure (d).

These grain boundaries are important in controlling the electrical properties of electroceramics, such as $SrTiO_3$, used in varistors and other devices. The structural work referred to here is part of an extended effort to understand the role played by grain boundary structure and defects in electrical properties.

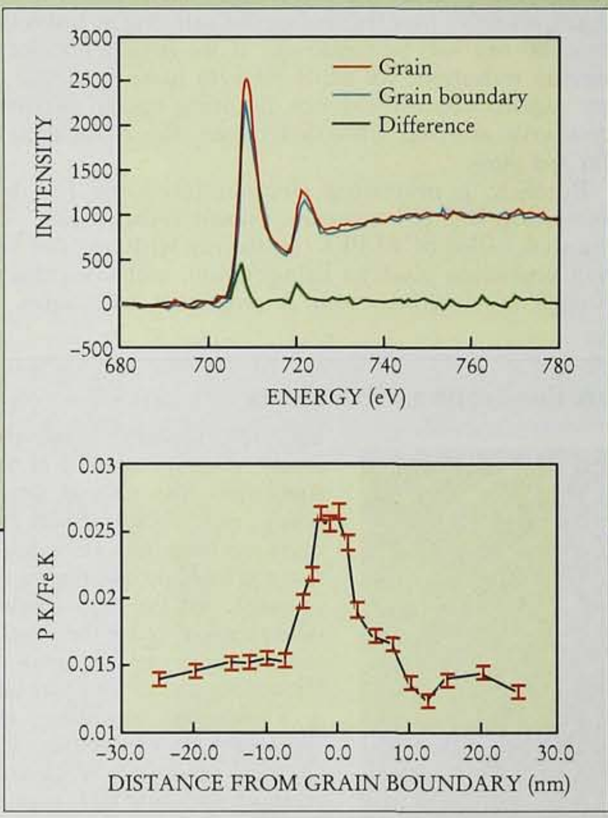
In the last few years, progress in quantitative matching has involved the use of cooled charge-coupled device cameras to obtain accurate digital measurement of the intensities. It has also involved the use of automatic image refinement methods in which the atomic positions and other parameters are adjusted to obtain reliable agreement between a set of experimental images and the calculations. Although this approach is not yet fully developed, the reliability of the fast electron diffraction theory is a firm base from which a more exact quantitative determination of interface structure is likely to be attained.

Box 3: Electronic Structure in Microscopic Volumes

When fast electrons pass through a solid, they experience energy losses that are proportional to the imaginary part of the inverse complex dielectric function $1/\varepsilon(\mathbf{q},\omega)$, where $\mathbf{q}$ is the wavevector and ω is the frequency. This function contains the full electronic and vibrational structure of the solid, albeit indirectly. Optical spectroscopy, which has been so widely used to characterize band structure, essentially observes the same function, though typically close to the regime where $\mathbf{q} = 0$. Studying band structure with electrons, rather than photons, is problematic because of the dynamic nature of scattering, which often involves multiple elastic and inelastic events. Its advantage is a consequence of the same physics: The strong interaction allows us to probe volumes as small as a few atoms.

A valuable recent development is the use of so-called near-edge structure—that is, fine structure in the energy-loss spectrum of the incident electrons just above an inner-shell excitation of the target atoms.[4] The appeal of this structural information is that the initial electron state is a well-understood, tightly bound atomic orbital, so that the near-edge structure is affected quite directly by the final state band structure.

Modeling these spectra is very similar to the analysis of XANES (x-ray absorption near-edge structure), but with the added advantage of examining microscopic volumes. The example in the figure was taken from a region near a grain boundary in iron, where the segregation of phosphorous is believed to weaken the mechanical strength of steels. The existence of phosphorous at the boundary is clearly seen with x-ray fluorescence as a small electron probe is moved across the boundary. The differential near-edge structure of the iron atoms at the interface implies higher 3d electron occupancy here, which gives a clue to the embrittling effect of phosphorous on the boundary.



SPECTROSCOPIC SIGNALS obtained by scanning a tiny electron probe across a grain boundary in steel, where the phosphorous has segregated. In the upper figure, the near-edge structure for the iron $L_{2,3}$ edge is traced by the electron-energy spectra of the grain (red) and grain boundary (blue): Their difference (green) indicates a change in the electronic configuration of iron at the interface. In the lower figure, the ratio of phosphorous and iron fluorescence signals clearly reveals the presence of phosphorous at the grain boundary. (Courtesy of Dong Ozkaya, Jun Yuan and Mick Brown of the University of Cambridge, UK.)

cannot claim to be an unbiased advocate of this method, being one of its inventors together with Steven Berger of Integrated Solutions Inc.) In box 5 on page 61, we see an example of this technique.

Projection lithography with ions or electrons is actually an old idea, but a severe problem had arisen with the method for obtaining contrast. In general, a patterned mask is illuminated to project a high-contrast image onto the wafer. In UV photolithography the contrast is obtained by absorption: A chrome layer is patterned on glass, which absorbs the light completely, even though the chrome is very thin.

A similar concept has been employed in projection electron lithography, but the mask must be thick enough to stop the relatively high energy electrons. Since the absorption distance for electrons in materials is rather high, this technique requires a thick mask with a high aspect ratio of thickness to feature size.

Worse, the mask must be a stencil, with open regions between the features. Note that high-energy electrons are used because of their shorter wavelength and hence better optical performance. Even if one could solve the difficult fabrication problems of such stencil masks, a more severe problem remains: Since the beam is stopped in the mask, the energy deposited in the mask is very high, and thermal expansion can create serious distortion.

In the SCALPEL approach, a thin mask is used simply to deflect the electron beam by means of differential elastic scattering between regions. A patterned film of tungsten, which has a large cross section for the elastic scattering of electrons, is spread on a membrane of weakly scattering silicon nitride. The back focal plane contains the angularly resolved scattering distribution of the electrons. The strongly deflected beam from the patterned regions is stopped by a back focal plane aperture, which is a massive object negligibly affected by the energy absorption. High image contrast is then obtained in the image, with the patterned regions being relatively dark. The first complete instrument, the "Scalpel Proof of Concept" machine, is now functioning at Bell Labs Lucent Technologies, and has demonstrated the ability to print 80 nm lines over large fields.[5] (See box 5 on page 61.)

Although a major development project is still required, the prospects for SCALPEL-based manufacturing of integrated circuits with 0.07 μm linewidth does not seem remote. Such tools could produce 64 gigabyte DRAMs (dynamic random-access memories) and microprocessors with 90 million transistors per cm^2 if they are based on conventional CMOS (complementary metal oxide semiconductor) technology, which has shown to be scalable to this dimension using direct-write electron lithography.

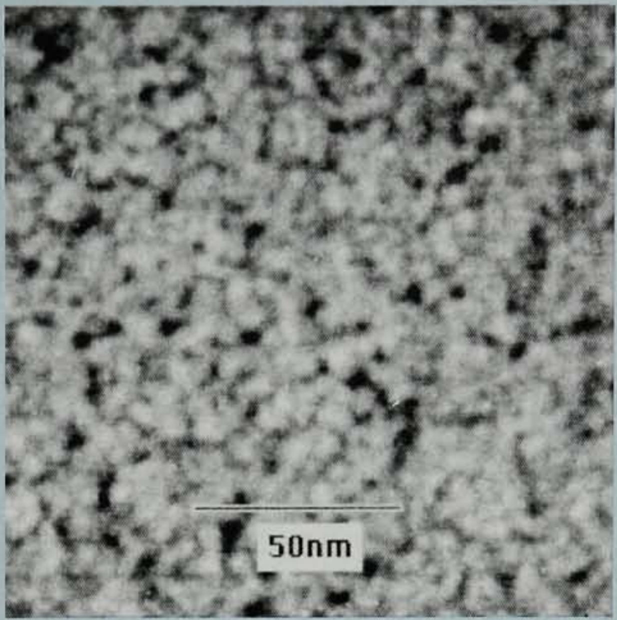
Given this potential performance, the need for novel electron devices to replace current technology is probably at least 20 years away, even though SCALPEL-based manufacturing could be realized sooner—in about 10 years' time. Notice the time scale for research. SCALPEL is

Box 4: Fluctuation Microscopy—Beyond Averaging

Diffraction methods have been enormously successful in solving the structure of crystalline solids. However, for amorphous solids the picture is murkier. The problem is that the loss of phase information in the diffraction pattern limits the real-space inversion to the pair correlation function (Patterson function). This function is very insensitive to medium-range order, but has been very successful in identifying the short-range order in amorphous materials. One attractive approach to overcome this critical limitation is to use electron microscopy for probing the local fluctuations in diffraction from amorphous solids. These fluctuations are sensitive to higher-order atomic correlations and much more sensitive to medium-range order than the averaged diffraction pattern. Fluctuation microscopy can examine the entire "micro" diffraction pattern as a function of position in real space or pick a controlled segment of Fourier space and form a dark-field image revealing spatial variations of scattering into the segment—a technique called variable coherence microscopy.

An example of variable coherence microscopy—as applied to a specimen of amorphous silicon—is shown in the figure. The patterns resemble those from laser speckling; however, when they are subjected to statistical analysis, nonrandom features and strong medium-range ordering emerge. When thermally annealed, the medium-range order is reduced, implying a transformation toward the more stable continuous random network structure.[6]

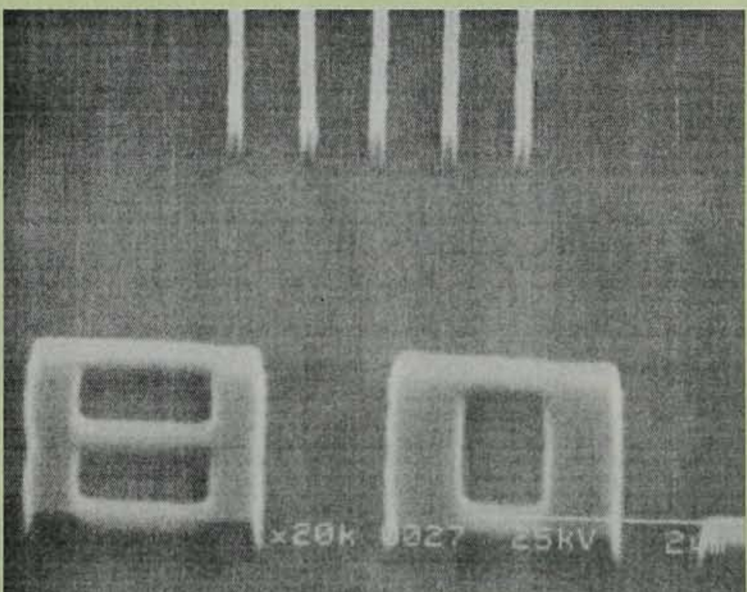
Statistical analysis of scattering in amorphous materials is very promising. Eventually, when resolution improves sufficiently (to around 0.05 nm), it could become possible to use tomography to directly determine the atomic structure of amorphous specimens. Such experiments would require instruments with both high resolution and the ability to tilt the specimen over a large angular range (about 90°), which is probably only possible with aberration correction.



Box 5: An Acre per Year of 0.1 μm Lines with SCALPEL

A wheat farmer would not consider harvesting one acre per year as high productivity, but when it comes to printing integrated circuits by lithography, this is the impressive rate at which a single "stepper" must operate to stoke the fire of the semiconductor industry. When printing features as small as 0.1 μm, the required exposure rate is in excess of 10 GHz, which is beyond the range of the fastest direct-write electron lithography tools. However, a parallel electron beam projection system, such as SCALPEL, can achieve the required exposure rates.

In the SCALPEL scheme, differential high-angle scattering of electrons by high-Z materials is used to impart a pattern to an electron beam of roughly 100 kV. The mask consists of a low-Z membrane about 100 nm thick, supporting a pattern of high-Z scattering material about 10 nm thick. The optical system demagnifies the image, which is created by a back focal plane filter, and removes the high-angle electrons. The use of a combined scanning projection system enables a strutted membrane to improve the mechanical rigidity.[2] (Picture courtesy of Lloyd Harriot and Alexander Liddle at Bell Labs, Lucent Technologies.)



now in the development stage and out of the research stage, but it is likely to be 10 years from production!

So, in conclusion, it seems that those green electron beams that Thomson identified have resulted in many important applications in visualizing and manipulating the structure of materials, and that these applications are only likely to be added to in the next few decades. Key aspects of such progress are likely to be the quantitative measurement and simulation of microscope images, allowing robust interpretation of microstructure, and the automatic control of sophisticated instruments, both for microscopy and high-volume chip production.

References

1. D. B. Williams, C. Barry Carter, *Transmission Electron Microscopy*, Plenum, New York (1996).
2. D. Hofmann, F. Ernst, Ultramicroscopy **53**, 205 (1994).
3. J. Zach, M. Haider, Optik **98**, 112 (1995).
4. N. D. Browning, J. Yuan, L. M. Brown, Physica C **202**, 12 (1992).
5. J. A. Liddle *et al.*, Jpn. J. Appl. Phys. **34**, 6663 (1995).
6. J. M. Gibson, M. M. J. Treacy, Phys. Rev. Lett. **78**, 1074 (1997). ■