Scanning electron microscopy for materials characterization
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Current materials are usually complex in chemistry, three-dimensional in form, and of rapidly diminishing microstructural scale. To characterize such materials the scanning electron microscope (SEM) now uses a wide range of operating conditions to target the desired sample volume, sophisticated modeling techniques to interpret the data. It also uses novel imaging modes to derive new types of information. These include depth-resolved three-dimensional data, and spatially resolved crystallographic data.

Introduction
The scanning electron microscope (SEM) is the most versatile and widely used electron beam instrument in the world. It owes its popularity to the easily interpreted nature of the micrographs that it generates, to the diversity of types of information that it can produce, and to the fact that images and analytical information can readily be combined. As this review demonstrates the use of the SEM for materials characterization is increasingly motivated by the desire to obtain not just images but quantitative information in two, or even three dimensions, about the microstructure, the chemistry, the crystallography and the electronic properties of the material of interest.

SEM for materials characterization
The basic mode of use of the SEM has always been in the imaging of surface topography, and 90% of the literature is still devoted to one aspect or another of this application. The increasingly high level of the performance of the SEM, in particular, makes it an excellent complement to high resolution transmission electron microscope imaging [1*,2] (as it provides the surface detail lacking in the TEM micrograph) or to scanning tunneling or atomic force microscopies, where it can provide images for comparison that are readily interpretable [3*]. The SEM is increasingly being used for in situ and dynamic experiments [4,5] because there is ample room in the specimen chamber for heating, cooling, tensile or other special devices and because such experiments provide uniquely valuable data.

Driven by the needs of the semiconductor industry, however, the predominant use of the SEM is as an analytical imaging tool for the metrology of integrated circuits. Here the requirement is to be able to extract from an image precise and accurate measurements of selected features for the control of the fabrication processes. This has been made feasible as a result of the development of detailed Monte Carlo models of the electron solid interaction occurring in the SEM [6**,7,8**]. It is now routinely possible to take an experimental image and then to compare it with a computed simulation of the same image, and by refining this match to iteratively deduce the parameters which describe the three-dimensional structure of the surface [9,10*]. Although difficult to apply to poorly characterized situations [11] the technique is quite successful when applied to the well defined geometry encountered in semiconductor devices, although problems arising from sample charging are still a limit to the accuracy that is possible.

While the SEM is usually considered to primarily be a tool for the visualization of surfaces, the electron beam does penetrate many micrometers into the sample. Because the penetration increases rapidly with the incident energy this effect can be exploited to add the missing depth dimension to imaging. For example, by choosing the energy of the incident beam and of the collected backscattered electrons, information specific to a particular depth beneath the surface of a specimen can be retrieved [12*]. A sequence of images obtained by appropriately varying the incident and exit energies then produces a sequence of optical sections of the sample which can be reconstructed into a full three-dimensional image. Because of the multiple scattering events experienced by every electron [13,14**] there is significant mixing of information between successive layers and so the vertical resolution is limited, but the method is a further important step in moving the SEM image from two into three dimensions and provides a non-destructive visualization tool of significantly higher lateral spatial resolution than X-ray microtomography.

In some parallel developments it has been shown that a sequence of cathodo-luminescence (emitted light) images produced from suitable samples, as the beam energy is varied, can also be processed to yield a stack of depth resolved slices through the specimen [15*,16]. This cathodo-luminescent (CL) signal is produced by the decay of the electron-hole pairs generated by the incident beam in a semiconductor or insulating material and the intensity of the CL signal, as well as the form of its spectrum,
depends on the type and concentration of dopant species in the material. So in this case the image is a map of the volume distribution of the chemistry as well as of the external and internal morphology of the material.

The electron-hole pair signal can also be detected from the sample by extracting it as a current—the ‘electron beam induced current’ (EBIC) signal—under the influence of a field from either internal P-N junctions or from a surface Schottky barrier. The EBIC signal provides a unique internal view of a semiconducting material, permitting direct visualization of all active junctions as well as of quantum wells, and electrically active defects in the material [17]. Once again if a sequence of images is obtained as a function of incident beam energy then depth resolved images can be generated [18*] which in this case represent a volume map of parameters such as the minority carrier diffusion length in the specimen.

A significant strength of transmission electron microscopy (TEM) as a materials characterization technique has been the availability of various modes of electron diffraction for the determination of crystal structure and for the imaging of dislocations, grain boundaries, and other lattice defects, crucial to the behavior of the material. The development of the technique of electron channeling [19] and the arrival of high brightness field emission guns on SEMs has now made it possible to obtain both crystallographic orientation information from sub-micrometer areas, such as is required for grain boundary studies [20]; and also to directly image dislocations in a bulk specimen [21]. An entirely different approach to the determination of crystallography in the SEM is the technique of electron backscattering patterns (EBSP). In this mode of operation the angular distribution of the backscattered electrons is imaged by a suitable detector and then analyzed automatically by a computer to yield the Miller indices representing the crystallographic orientation. A spatial resolution of the order of 100 nm is possible [22*] with an angular precision of better than one degree [23**]. In fact, with careful experimental control angular rotations as small as 0.01 degrees can be detected, which corresponds to an elastic strain within the sample of only about 0.02% [24**], a value typical of the magnitude of the strains found in high quality epitaxial films. A unique feature of this technique is the ability to synthesize an ‘Orientation Image’ in which, for example, the three colors of an RGB (red-green-blue) color-coded display are employed to represent the spatial variation of the three Euler angles describing the crystal orientation. These orientation images reveal clearly, and display quantitatively, effects such as texturing [25*], recovery and recrystallization [26] and grain boundary misorientations [27*]. Although the time taken to derive such an image is often many hours the detail and quality of the information is unmatched by any other technique and it can be claimed fairly that the crystallographic capabilities of the SEM now exceed those of the TEM in their versatility and power.

The use of the SEM at low beam energies, that is to say below 5 keV, has now become the preferred mode of operation for many applications [28]. The attraction of the technique is that it permits the successful observation of materials which are difficult or impossible to image satisfactorily at higher beam energies. This is, in part, because the increase in secondary electron emission at low energies can result in a state of dynamic charge balance at the specimen so that poorly, or nonconducting, specimens can be imaged without net charge build-up [29**]. It is therefore not necessary to use any surface coating to confer conductivity allowing the true surface structure of the sample to be observed. At the same time the reduction in beam energy results in a decline in the depth of penetration of the electrons so that radiation induced damage is localized at the surface rather than spread through a large volume. The LVSEM (low voltage SEM) is therefore well suited for the study of polymers [30-32] and other fragile and exotic materials such as snow crystals [33**].

Microanalysis is an essential component of materials characterization and has been an important application of the SEM since energy dispersive X-ray spectrometers first became available thirty years ago. However, the demands placed on microanalysis in the SEM are also rapidly changing. Historically, microanalysis was based on the assumptions that the specimen to be analyzed was chemically homogeneous over at least the beam interaction volume of a few micrometers diameter, that the sample was flat, and that the surface was smooth. For the problems encountered in today's materials science none of these assumptions are likely to be valid and so new procedures for obtaining and interpreting data are required. With the continual reduction in the scale of microstructure the spatial resolution of an analysis is now a crucial issue. While the fundamental limits set by the electron–solid interactions remain, the application of Monte Carlo simulations demonstrate that small features, such as a monolayer of an element at a grain boundary, can reliably be detected under optimized conditions [34**]. An alternative route for improving spatial resolution is the use of low beam energies which offer much reduced beam interaction volumes but this raises the practical problem that only low energy X-ray lines are accessible and so peak overlaps become a major limitation. However, new bolometric device technology for X-ray spectrometers [35**] offer sufficiently high energy resolution such that all probable peak overlaps can be separated. Some novel strategies for microanalysis are also under development. For example, the secondary electron image can reveal, in a quantitative manner, the concentration of dopants in a semiconductor [36**] even at levels corresponding to only about one part per million, far below the concentrations required for X-ray analysis. Secondary electron imaging used in this way is, in fact, closely related to Auger analysis because it is a measure of the total electron yield [37*]
and if it can be made fully quantitative, then it may be a promising new tool for characterization.

The single most exciting recent contribution of the SEM to materials characterization has been through the development of the environmental (ESEM) or nature SEM (NSEM). In these instruments the vacuum condition around the specimen has been relaxed so that the conventional high vacuum has been replaced by a gaseous environment in which the pressure can be as high as 20 torr (2,300 Pa). The presence of a gas, typically saturated water vapor or moist air, has significant effects on both the imaging mechanisms and on the types of sample that can be examined. Ion production in the gas results in dynamic charge neutralization of the specimen permitting poorly conducting materials to be successfully imaged at high beam energies (38*,39*,40) as well as producing novel imaging effects such as the ability to see to the bottom of deep cracks and holes [41**]. Most importantly the ESEM and NSEM configurations liberate the user from the problems associated with preparing specimens for observation in conventional high vacuum SEMs. An enormous range of real-world problems immediately become accessible for examination in this way for example, the in situ observation of corrosion [42*], the formation of cement [43*], the study of pharmaceuticals [44] and common household and personal products [45*]. As most of the standard imaging and analysis modes of the SEM can also be performed in the gaseous microscope, the potential scope of this machine for real materials characterization is considerable. The interaction of the electron beam with the gas can even be used to deposit metal on the specimen surface for the fabrication of connector lines [46**] or to form micro-miniature three-dimensional structures [47**]. The SEM as a tool for materials characterization thus becomes in turn a new tool for the fabrication of still more complex materials.

Conclusions
While the basic capabilities of the SEM have remained unchanged, the combination of innovative operating strategies and the use of Monte Carlo, or other, modeling techniques has resulted in a significant enhancement in the variety and quality of the data that can be obtained from materials. Thus, while the complexity of the task of microcharacterization continues to increase the SEM remains fully capable of meeting these challenges.

References and recommended reading
Papers of particular interest, published within the annual period of review, have been highlighted as:

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Characterization techniques


Beautiful application of the SEM to the study of the fragile and complex microstructure of snow, ice and frost. A technical tour de force.

34. Wilton AR: Monte Carlo and finite element calculations of X-ray production at interfaces in bulk materials. Ultramicroscopy 1996, 66:117-131. A demonstration that the spatial resolution limit to microanalysis set by electron–solid interactions does not prevent the observation of small features provided that conditions are properly optimized.


41. Newbury DE: Imaging deep holes in structures in the ESEM. SCANNING 1996, 18:474-483. The conversion of secondary electrons to ions in the gas of the ESEM specimen chamber makes it possible to form satisfactory images from the bottom of holes several millimeters in depth.


