Nano Characterization of Materials

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Material and device characterization is challenged by continuously decreasing device dimensions placing significant demands on characterization instruments and measurement interpretation. The trend in many techniques is clearly toward characterization of smaller dimensions. Among the myriad of characterization techniques in use today, I discuss recent advances in probe microscopy, interferometric microscopy, transmission electron microscopy, electron holography and tomography, nano secondary ion mass spectrometry, atom probe ion field ion microscopy and X-ray tomography. All of these have made significant advances and have produced very impressive results. For example, TEM is now able to generate images with 0.05 nm lateral resolution, allowing display of individual atoms. Probes in conjunction with magnetic fields have demonstrated vertical resolution of 0.0015 nm. Progress in developing further advances in nm dimensional characterization will, no doubt, continue to satisfy the demand for such measurements.

Introduction

Nanotechnology has become a much-used and sometimes abused word in the past decade or so, although the term has been around for over 35 years having been coined by Taniguchi in 1974 (1). He plotted the accuracies of machine tools versus time in 1984 and predicted that by the year 2010 accuracies in the nm range would be required for precise measurements (2). We have clearly passed this value with nano measurements able to “see” features as small as 0.05 nm! Such measurements fall into two distinct categories: vertical and horizontal measurements, illustrated in Fig. 1, i.e., how small can Δz and Δx be to be measured accurately. Some techniques are capable of very high vertical and nominal horizontal resolutions. For example, interferometric microscopy has vertical resolutions on the order of 0.1 nm, but the modest lateral resolution of ~ 0.25 μm is limited by the wave nature of light. Electron beam techniques, especially transmission electron microscopy, have exceedingly high lateral resolutions approaching 0.05 nm, but provide little depth information. Such measurements allow individual atoms to be detected. Scanning and atom probes can provide both high vertical and lateral features with sub-nm dimensions, allowing atomic resolution.

![Figure 1. Feature sizes to be determined by nano characterization techniques.](image)
Measurement techniques show a wide lateral resolution range in Fig. 2. Leading-edge techniques for ultimate resolution are transmission electron and probe microscopies. As shown in Fig. 2, for resolutions to about 10 nm, electron beam and scanning probe techniques dominate. Beyond that, there is a plethora of methods. I will merely describe a few of these: probe microscopy, interferometric microscopy, transmission electron microscopy, electron holography and tomography, nano secondary ion mass spectrometry, atom probe ion field ion microscopy, and X-ray tomography. The ideal microscope reveals the position and identity of all atoms in a specimen. This is not possible in any scanning probe instrument or electron microscope, but atom probes approach this ideal.

![Figure 2. Best lateral resolution for various characterization techniques. TEM: transmission electron microscope, FESEM: field emission scanning electron microscopy, Conf.: confocal, EDS: energy-dispersive spectroscopy, SIMS: secondary ion mass spectrometry, RBS: Rutherford backscattering spectroscopy, XPS: X-ray photoelectron spectroscopy.](image)

**Probe Microscopy**

In scanning probe microscopy (SPM) a sharp tip is scanned across the sample surface to obtain two- or three-dimensional images of the surface at nanometer or better lateral and/or vertical resolution (3). In the extreme, one can obtain lateral resolutions on the order of 0.1 nm and vertical resolution of 0.01 nm or better in some cases. The original application of SPM was the scanning tunneling microscope (STM), built in 1981 by Binnig and Rohrer to study atomic surfaces in greater detail than was possible at the time (4). The tunneling current depends very sensitively on the distance between the tip and the surface, so measuring this current change as the tip was scanned over a sample allowed objects as small as atoms to be imaged. A myriad of SPM instruments has been developed over the past decade, and one can sense current, voltage, resistance, force, temperature, magnetic field, work function, light, and so on with these instruments at high resolution. The operation of the instruments is generally based on detecting the near-field image. If the scientific community ever needed to be convinced that nanotechnology was real, Eigler and Schweizer provided the evidence. Working at IBM’s Almaden Research Center, they used an STM to position individual atoms on a metal surface at liquid He temperature. In possibly the most famous image in the history of nanotechnology, they wrote the letters IBM with 35 xenon atoms on a nickel surface, shown in Fig. 3(a) for historical reasons (5). A more recent atom motion image in Fig. 3(b) shows the first atomic pattern created with an atomic force microscope (AFM) by laterally manipulating individual atoms at room temperature by inducing the in-plane interchange of Sn atoms (brighter protrusions in Fig. 3(b)) with the adjacent Ge atoms (6). The Sn atoms are embedded in the surface plane by substituting some of the Ge atoms and are strongly bound to the underlying atomic plane. SPM has been described in many publications (7) and here I only discuss magnetic exchange force microscopy as a recent example of the power of this technique.
Figure 3. (a) STM images of individual xenon atoms on a nickel surface manipulated with a STM. Each letter measures 5 nm from top to bottom. It took Don Eigler and Erhard Schweizer 22 hours on 9/10 November 1989 to obtain these images. Figure reproduced from ref. 5; (b) AFM-moved Sn on Ge surface. After Sugimoto et al. (6).

**Magnetic Exchange Force Microscopy (MExFM)**

The concept of magnetic exchange force microscopy is shown in Fig. 4 using the example of antiferromagnet nickel oxide, with neighboring planes aligned antiferromagnetically with nickel spins of alternating opposite orientations. For MExFM measurements, a cantilever with an iron-coated tip is scanned above the surface. An external magnetic field maximizes the sensitivity of the tip apex to the out-of-plane component of the canted spins of the Ni atoms. Purely chemical and structural contrasts reflect only the arrangement of nickel and oxygen atoms. The additional magnetic exchange interaction between the spins of the Fe atom at the tip apex and the Ni atom directly below provides an additional contrast modulation between neighboring rows of nickel atoms (8).

Force is detected by the tapping-mode technique with the cantilever self-oscillating with constant amplitude and tip–sample interactions shifting the cantilever frequency from the resonance frequency of the free cantilever. During x-y plane scans, the frequency change remains constant by adjusting the z position of the tip relative to the surface, permitting atomic resolution on conducting and non-conducting surfaces in the non-contact regime, with height differences in the topographic image reflecting variations of the short-range forces between the tip atom and the atomic species at the surface. The corrugation data in Fig. 4 combine the atomic resolution capabilities of atomic force microscopy with spin sensitivity, revealing the arrangement of both surface atoms and their spins simultaneously. From the line section, the chemical apparent height difference between nickel and oxygen is about 0.0045 nm. For smaller separation the additional apparent height difference between Ni of opposite spin orientations due to the magnetic exchange interaction with the spin of the iron tip is 0.0015 nm. These images illustrate the remarkable lateral and even more the vertical spatial resolution of probe measurements.
A second magnetic example in Fig. 5 shows spin-polarized STM (SP-STM) constant-current images of single cobalt atoms (9) with varying heights and shapes (Figs. 5a,b). Three distinct cases are marked by boxes in Fig. 5a: the Co atoms appear higher when they are located on bright substrate manganese atom rows (top) and lower on dark manganese rows (bottom). In addition to these height variations, the shape of the atoms appears to be different on bright and dark manganese rows. Figure 5c shows a magnified view of two cobalt atoms at positions where the manganese magnetic moments underneath point exactly upwards and downwards. Depending on which of these two possible orientations occurs, the cobalt atom appears either rotationally symmetric with its maximum height at its centre (left) or elongated with two lobes and a central minimum (right). Because in equivalent images acquired with a non-magnetic tungsten tip all cobalt atoms appear identical, these variations in height and shape are of magnetic origin.

Figure 5. SP-STM of single cobalt atoms on manganese. a: periodic stripes indicate the magnetic contrast of adjacent atomic rows. The height/shape of the Co atoms depend on their position on the manganese. b: perspective view of the manganese spin spiral, Co dimer indicated by a black cross. c: Co magnetic moment up and down and the respective line profiles. After Serrate et al. (9).
Optical Characterization

Phase-Shift Interferometry

Interferometric microscopy is a contactless method to determine horizontal and vertical features of a sample. An interferometer splits a beam from a single source into two separate beams and then recombines them. The resulting interference pattern is recorded as an interferogram. Commonly, in interferometers one beam is reflected from the object under test and the other beam is reflected from a reference mirror. The beams are recombined, creating bright and dark bands called “fringes” that make up the interferogram. The interferogram is recorded with a CCD camera and processed with interferometric phase-mapping programs. The most popular interferometric measurement techniques are: Phase Shift Interferometry (PSI), Vertical Scanning Interferometry (VSI) and Enhanced VSI (EVSI). PSI uses a monochromatic light source, typically measures smooth surfaces and is very accurate with sub-nm vertical resolution. However, PSI cannot obtain a correct profile for objects with step height changes exceeding $\lambda/4$. Typically, the sample is imaged through a microscope giving a maximum lateral resolution of conventional microscopy of $\sim 0.5 \lambda/NA$, where NA is the numerical aperture. The $z$ resolution, however, is determined by the ability to interpret fringes using phase modulation techniques. The vertical resolution is around 1 nm. Phase modulation techniques allow phase calculations to better than 0.01 of two neighboring fringes or vertical resolutions of 0.1-1 nm.

One method of removing the height ambiguity is to make measurements at two wavelengths $\lambda_1$ and $\lambda_2$. Now the limitation in height difference is $\lambda_e/4$, where $\lambda_e$ is the effective wavelength $\lambda_e=\lambda_1\lambda_2/|\lambda_1-\lambda_2|$. A disadvantage of this approach is degradation in the precision of the measurement by the ratio $\lambda_e/\lambda$. Multiple wavelength interferometry works well on some samples, but for rough samples noisy data points lead to errors. For microscopes with high magnification and high numerical aperture, the upper and lower surface of a sample discontinuity may not both be in focus at the same time. This is a further source of errors. Recently, aspects of PSI and VSI have been combined to take advantage of the strengths of each. First, for each pixel of the detector, the best-focus frame position is found by locating the best contrast of interference intensity distribution along the vertical scanning direction. Second, the PSI technique is applied to intensity distribution around the peak to achieve high resolution measurement.

Interferometric microscopy is implemented in several ways; two of these are: the Mirau interference microscope and the Linnik interference microscope. The Mirau interference microscope is schematically illustrated in Fig. 6. The principle of the device relies on placing a reflection reference mirror in the center of the objective lens, and interposing a half mirror between the objective lens and the specimen. These components are so arranged that an interference pattern appears if the system is focused upon the specimen. Light is incident on the microscope objective. Some is transmitted to the sample; the remainder is reflected by the beam splitter to the reference surface. The light reflected by the sample and the reference surface are combined at the beam splitter and interfere. The resulting interference fringes give the difference between the sample surface and the reference plane. The reference surface, objective lens, and beam splitter are attached to a piezoelectric transducer translating the reference surface to vary the phase of the reference beam.
The Linnik interference microscope is a *Michelson interferometer*. A plane wave front from a coherent, monochromatic light of wavelength $\lambda$ is incident on a beam splitter. Part of the beam is transmitted to a stationary reference mirror and part is transmitted to the sample. Both beams are reflected to the beam splitter where they combine and are transmitted to the detector. The phase change is introduced by varying the sample-beam splitter distance with a piezoelectrically controlled table. The Linnik interferometer utilizes a high magnification objective lens. Because uniform objective lenses are difficult to manufacture, only a small number of such instruments have been marketed.

An extension of optical sample height measurements uses white light in a Linnik interferometer. With a white light source, the interference fringes with the best contrast obtain only when the two paths in the interferometer are equal. Hence, if the path length to the reference mirror in the interferometer is varied to give maximum fringe contrast, that path length corresponds to the distance to the sample surface. There are no height ambiguities, especially since the sample is in focus when the maximum fringe contrast is observed. Height variations up to 100 µm can be measured in this manner. In an interference microscope, where height measurements are the main concern, lateral resolution limits take on a somewhat different meaning. The blurring of small objects leads to edge smoothing at height steps, reducing the accuracy of the height measurement.

Figure 7 shows the center-to-edge film thickness variation of a nominally 80-nm thick silicon nitride film (10). Metrology of the < 2.5nm range in film thickness, when combined with surface topography mode, allows for control of etch and polishing operations in semiconductor processing.

Figure 7. Variation in thickness of a nominally 80-nm thick Si$_3$N$_4$ film on a silicon wafer by measurement site, using the pupil-plane technique. After de Groot and de Lega (10).
Electron Beam Characterization

Transmission Electron Microscopy (TEM)

In his 1960 paper *There’s Plenty of Room at the Bottom*, Feynman stated “…. the electron microscope is 100 times too poor….I put this out as a challenge: Is there no way to make the electron microscope more powerful?” (11) Well, the TEM community has, of course, worked on this problem for many years and through constant improvements has now reached ~0.05 nm lateral resolution. A joint project, the *Transmission Electron Aberration-corrected Microscope*, between Lawrence Berkeley National Laboratory, Argonne National Laboratory, Oak Ridge National Laboratory, and the University of Illinois, as well as FEI and CEOS companies was started in 2004 to design and build a TEM with a spatial resolution below 0.05 nm. It was built and achieved the 0.05 nm resolution target in 2009. Other TEM producers, e.g., JEOL, Hitachi, Nion, have also developed such microscopes. In the past, only atom columns and extended defects, e.g., stacking faults and dislocations, could be observed by high-resolution electron microscopy. Direct imaging of single-defect atoms was not possible due to noise and resolution limitations.

In a dedicated scanning TEM (STEM) the effective source size of the electron emitter is de-magnified by the condenser lens system and transferred to the objective lens to focus the beam into a small probe in its back focal plane, where the small electron probe is rastered across an electron transparent specimen. The electrons transmitted through the specimen are then recorded by various detectors as a function of probe position on the sample. Detectors commonly used in a STEM are annular dark-field (ADF), on-axis bright field and secondary electron detectors as well as energy-dispersive X-ray spectrometers and energy-loss spectrometers. In a dedicated STEM most of the different detector signals can be acquired simultaneously with pixel-to-pixel correlation.

The resolution limiting factor in STEM has historically been spherical aberration of the probe forming lenses, particularly the objective lens. Third-order aberration correction revolutionized electron microscopy, allowing materials characterization with unprecedented detail, due to the possibility of using electron probe sizes well below 0.1 nm, leading to significantly increased lateral spatial resolution and increased signal to noise ratio, enabling single atom sensitivity, and higher depth sensitivity providing higher resolution in the vertical direction.

The capability of today’s TEM ability is illustrated in Fig. 8 (12). The TEM micrographs show four lattice images of a gold nanobridge connecting two gold crystals. The images are recorded in the TEM mode at 1 s exposures at time intervals of 1.5 s. The four images in Fig. 8 show the structural evolution of the crystals recorded over 4.5 s at different focus values. Closer inspection of the images reveals a wealth of structural changes at the nanobridge/vacuum interfaces that were triggered by electron-beam excitation. The black arrows (solid circles) highlight the release of a single atom from a 2-atom column (Figs. 8a,b) leaving a single atom behind (Figs. 8c,d). The red arrows (ellipses) mark a row of thirteen 2-atom columns. In a sudden burst, six columns disappear during TEM observation (compare Figs. 8c,d images).

Another example of high-resolution TEM images is shown in Fig. 9, where Ge self-interstitial atoms were introduced into Ge single crystals by electron irradiation (13). Figure 9 (a) shows the Ge lattice with interstitial atoms identified. The sample is only a few atomic layers thick. Even the 0.14 nm dumbbell distances can be resolved well beyond the Rayleigh resolution criterion. The interstitial atoms appear at various locations in the projected Ge unit cell as additional contrasts in the void between the lattice columns.
(Figs. 9 (b) to (e)). However, these contrasts appear and disappear from frame to frame when image series are recorded with a time of interval of one second. This direct observation of single-atom diffusion in Ge for migration barriers of less than 1 eV, suggests that the electron beam assists interstitial migration. The atomic column and single-atom positions were determined by fitting Gaussians with subpixel accuracy to the two-dimensional intensity distributions in the images.

![Figure 8](image1.png)

Figure 8. Four sequentially recorded TEM lattice images of a gold nanobridge. The four images shown are recorded in time intervals of 1.5 s. Black arrows (circles): (a,b) 2-atom column and (c,d) single atom. Red arrows (ellipses): thirteen 2-atom columns, some of which disappear in d. After Kisielowski et al. (12).

![Figure 9](image2.png)

Figure 9. TEM images of a thin Ge crystal [black arrows show occupied interstitial sites, red arrows (circles) show column vibrations during the acquisition time. Magnified areas where an interstitial atom is observed, (b) and (c) in T sites, (d) in an H site that overlaps with a bond-centered site, (e) in an off-center site. After Alloyeau et al. (13).
A bright field STEM image is identical with images recorded by high-resolution TEM (HRTEM), which are based on diffraction interference or phase contrast. Through the use of ADF detectors, Rutherford scattering by the atomic nuclei is the predominant contrast mechanism. This is an incoherent signal because large detector sizes cause an integration of phase contrast effects, i.e., different Bragg reflections are integrated to form an image based on total scattered intensity. Since the cross section is roughly proportional to the square of the atomic number of the scattering element, this technique is referred to as Z-contrast imaging or high angle ADF (HAADF) imaging. The image formation is incoherent, making images directly interpretable without the need of extensive image simulations.

In STEM Z-contrast imaging, an electron probe is scanned across a thin specimen, and the Z-contrast image results from mapping the intensity of electrons scattered at high angles (14). The scattering is predominately incoherent and proportional to the square of the atomic number, Z, of the scattering atom. This contrast mechanism yields images where even small changes in average number are easily discriminated. The high scattering angles break the coherence in the transverse plane, giving an increasing intensity with thickness with a brightness determined by their mean square atomic number \( \bar{Z} \). This chemical sensitivity enables different elements to be distinguished at the atomic scale.

An early example of this measurement is the interface between a thin HfO\(_2\) layer and a silicon substrate grown by atomic-layer deposition. Electron energy-loss spectroscopy reveals a very thin silicon oxide layer between the HfO\(_2\) and the Si substrate. Small spots of bright contrast, identified as single Hf atoms embedded in the SiO\(_x\) structure, were observed throughout this interlayer in multiple different positions (15). Using aberration correction, smaller electron probe sizes become available through increase of the illumination angle, allowing thinner sample sections to be in focus leading to higher depth sensitivity. Hence, the acquisition of through focal series effectively becomes equivalent to an optical slicing of the TEM sample and such images can then be used for three dimensional reconstructions of the structure. Single Hf atoms are in focus at different depths in the recorded image stack. A final reconstruction of the three dimensional interface clearly shows the location of individual HF atoms (16).

Figure 10. The atomic structure determined by the histogram analysis. Part of a DFT simulation of a single BN layer containing the experimentally observed substitutional impurities overlaid on the corresponding part of the experimental image. Red, B; yellow, C; green, N; blue, O. After Krivanek et al. (17).

Until recently, neither electron microscopy nor any other experimental technique was able to resolve and identify all the atoms in a non-periodic material consisting of several atomic species. Recent research shows that annular dark-field imaging in an aberration-corrected STEM optimized for low-voltage operation can resolve and identify the chemical type of every atom in monolayer hexagonal boron nitride with substitutional defects. Three types of atomic substitutions were found and identified: carbon substituting for boron, carbon substituting for nitrogen, and oxygen substituting for nitrogen. The substitutions caused in-plane distortions in the boron nitride monolayer of about 0.01 nm, which
were directly resolved, and verified by density functional theory calculations. The results demonstrate that atom-by-atom structural and chemical analysis of all radiation-damage-resistant atoms present in, and on top of, ultrathin sheets has become possible (17). Figure 10 shows the atomic structure of the impurity atoms identified in the monolayer, superimposed on the deconvolved experimental image. The BN monolayer was bordered by thicker regions, which included carbon and heavier atom impurities imaged as isolated bright atoms. Carbon atoms are only seen to substitute for B–N pairs, not for individual boron or nitrogen atoms, but oxygen substitutes for single N atoms. The atomic positions in the diagram were determined by a density functional theory relaxation.

Electron Holography

Electron holography, conceived by Gabor (18) to overcome the spherical aberration of the TEM objective lens, is applied to map potential distributions in semiconductor devices (19). In electron holography the relative phase of the electron beam after passing through the specimen is determined by comparison with a coherent reference wave. Unlike conventional electron microscope images, represented by the electron wave intensity with no phase information, electron holography allows both phase and amplitude of the coherent wave front to be determined. The phase shift is sensitive to local variations in magnetic and electrostatic potential, allowing quantitative information about magnetic and electric fields in materials and devices with a spatial resolution that can approach the nm scale to be determined. The reconstructed phase image provides direct imaging of the electric and magnetic potentials within the sample. Several electron optical geometries have been developed for making electron holograms, but the most popular, the off-axis, image plane geometry, is illustrated in Fig. 11(a). This holographic operating mode is easily obtained in commercial FEG TEMs, and has been used almost exclusively in recent electron microscopy studies. However, at least 20 different forms of electron holography using conventional TEM and scanning TEM (STEM) have been identified (20).

![Electron Holography](image)

Figure 11. (a) Schematic of electron holography, (b) MOSFET electrostatic potential contour maps. The separation between adjacent contour lines is 0.1 V. After Han et al. (21).

In off-axis holography a ~0.3–0.5 μm diameter conductive fiber, e.g., a gold-coated quartz fiber, the electron biprism (22), is positioned in the imaging lens perpendicular to
the electron beam. A thin TEM specimen, ≤ 500 nm thick to ensure that the original hologram is not degraded by multiple electron scattering effects, is placed over one side of the image field. A field emission electron gun provides a highly coherent source of electrons. In reality, the source is never perfectly coherent, but the degree of coherence must be such that an interference fringe pattern of sufficient quality can be recorded within a reasonable acquisition time, during which specimen and/or beam drift must be negligible. A positive voltage (50 V to 200 V) on the biprism causes overlap between the scattered or object wave and the reference wave, leading to finely spaced holographic interference-fringe pattern formation in the TEM image. The biprism voltage tilts the ‘reference’ electron wave through vacuum with respect to the electron wave through the specimen. The two waves overlap and interfere.

The interference fringes are changed in position and contrast, depending upon how the specimen affects the electron beam. The development of high-brightness field-emission guns (FEG) has been a major factor to implement electron holography. Off-line optical methods, traditionally used in wave function reconstruction from electron holograms, have been largely replaced by digital processing of electron holograms owing to the advent of the slow-scan charge-coupled-device (CCD) camera (23). In the absence of strong dynamical electron diffraction effects, the phase component is directly related to electrostatic potential, making electron holography useful for 2-dimensional profiling of electrostatic potentials in semiconductor structures. Reconstruction of the phase of the electron wave from the hologram involves Fourier transformation, selection of the sideband in diffraction space and inverse Fourier transformation to produce amplitude and phase maps. The phase yields the potential provided the sample thickness is known. For example, it is possible to display potential contour maps of semiconductor devices without and even with bias by carefully attaching contacts to the TEM specimen. Figure 11(b) shows the cross section and the potential contours within a MOSFET. This figure clearly shows the source/drain, gate, and gate spacer regions.

Proper sample preparation is very important. The sample must be thinned to be electron transparent. The specimen thickness must be accurately known for quantitative measurements of electrostatic and magnetic fields. Focused ion beam (FIB), commonly used for TEM sample preparation, produces sample damage making quantitative holographic analysis unreliable. The preferred method is wedge polishing, followed by FIB in-situ sample lift-out, and back surface low-energy Ar ion milling, but conventional specimen preparation without inducing FIB artifacts is too time consuming for industrial application. This may bring the method closer to becoming a standard analysis tool for future semiconductor metrology (24).

Holographic phase also provides information other than potentials. For example, one can determine the two-dimensional carrier concentration profiles. This has led to studies of dopant atom movement during laser annealing. In one study, it is shown that a short-time laser anneal does not change the doping profile (25). In the same study electron holography during failure analysis was used to show drain boron dopant depletion near a shallow trench isolation oxide. The dependence of the phase shift on the inner potential can be used for mapping the projected 2-D composition of a specimen. The difference in the mean inner potential of Si and Ge allows for quantitative measuring of the Ge concentration in a SiGe alloy on a sub-nanometer scale, illustrated in Fig. 12 (26).

Holography can characterize materials differing only slightly in their density with insufficient contrast for conventional bright-field or dark-field imaging. However, the mean inner potential of the materials may differ sufficiently to be detected in the phase image (27). An interesting variant of off-axis electron holography provides strain distributions
in semiconductors. It uses the electrostatic biprism to form a dark-field electron hologram by interfering with diffracted electrons scattered in strained and unstrained regions of the specimen (28). A further extension of electron holography is the combination of electron holography with electron tomography to characterize electrostatic and magnetic fields in nano-structured materials with nm spatial resolution in 3-D. Both the electrostatic phase shift and the magnetic phase gradient recorded using electron holography satisfy the projection requirement for electron tomographic reconstruction (29).

Strain in semiconductor devices can be determined with Raman, X-ray diffraction, and dark-field inline holography which relies on data collected in real space, but, in contrast to off-axis holography does not derive the strain information from the position of interference fringes of the scattered electron wave, but instead from variations in the intensity of dark-field TEM images with defocus (30). It is also possible to use a combination of the moiré technique and off-axis electron holography (28). A coherent electron beam illuminates the sample in a diffraction condition for a certain set of lattice planes. The sample is composed of a zone of an unstrained crystal of known lattice parameters, adjacent to a strained crystal, in a similar orientation and diffraction conditions. The two diffracted beams interfere and their phase difference depends on the elastic scattering and the geometric phase. For samples of uniform thickness, the former is a constant term, while the latter encodes the strain information through phase gradients.

Figure 12. SiGe layers with different Ge content. (a) Bright-field image exhibiting high contrast but only medium resolution. (b) High-resolution bright-field image exhibiting atomic resolution but poor contrast. (c) Phase image exhibiting high resolution (0.5 nm) as well as reasonable contrast. (d) Linescan from the phase image (c) clearly shows the Ge concentration steps in the Si\(_{1-x}\)Ge\(_x\) stack. After Lichte et al. (26).
Electron Tomography

Tomography is the cross-sectional imaging of an object from either transmission or reflection data collected by illuminating the object from many different directions. “Tomography” is derived from the Greek words *tomos* (slice) and *graphein* (to write). In tomography, a series of projection images are used to calculate a three-dimensional reconstruction of an object. Conventional TEM exhibits dynamic contrast changes due to crystal orientation and sample tilt angle making it difficult to visualize crystal defects. In recent studies, three-dimensional observations using electron tomography have been applied to not only the life science but also material science and semiconductor devices (31). Electron tomography provides nm-scale resolution in three dimensions. The 3-D structural information is reconstructed digitally from a tilt series of 2-D projections. The tilt-series is then processed off-line with back-projection techniques to reconstruct the “original” 3-D structure (32).

The technique was recently applied to a study of defects in strained Si MOSFETs (33) with SiGe in the recessed source/drain. The MOSFET channel in <110> direction on the Si (100) surface was studied with electron tomography and annular dark field (ADF) STEM techniques. The samples were ~200 nm thick. The STEM images were captured for tilt angles ranging from -60 to +60° (in 2° steps) at 200 keV. The defects were viewed from various directions: perpendicular to the channel direction, parallel to the channel and 45° from parallel to the channel direction. Two defects were confirmed: defect A is along the (111) plane from the edge of SiGe S/D and defect B is along the <110> direction. Figure 13 shows a schematic diagram of the MOSFET and sliced image of the cross section at the (111) plane. The data confirm that defect A grows on the (111) plane from the left edge of the SiGe/Si interface and defect B grows from the right edge of the SiGe/Si interface along the (1T1) plane. The origin of each defect is on the edge of the SiGe/Si interface and growing along different {111} planes.

![Figure 13. MOSFET schematic and sliced image of the cross section at the (111) Plane. After Kudo et al. (33).](image)

Ion Beam Characterization

Nano Secondary Ion Mass Spectrometry (Nano SIMS)

SIMS is based upon the sputtering of atomic layers from the surface of a sample by a primary ion beam. The primary ion impact triggers a cascade of atomic collisions leading to atom, molecule fragments and ion ejection. The secondary ions are characteristic of the composition of the analyzed area. They are separated according to their mass, and an im-
age containing quantitative information is formed for a selected mass. SIMS reveals elemental and isotopic surface composition. It is one of the most powerful and versatile analytical techniques for semiconductor characterization with detection limits for some elements in the $10^{14}$ to $10^{15}$ cm$^{-3}$ range if there is very little background interference signal. Lateral resolution of conventional SIMS is typically 100 µm but can be as small as 0.5 µm with depth resolution of 5 to 10 nm. Cesium (for negatively charged secondary ions) and oxygen (for positively charged secondary ions) are commonly used excitation ions. Other non-reactive primary ions like Ga or Bi, widely used in liquid-metal ion sources in focused ion beam systems with lateral resolutions below 100 nm, yield 100-1000 times lower signal intensities for elements.

**Nano SIMS** is a new generation of ion-microprobe combining high lateral and spectral resolution with high sensitivity. The coaxial lens allows the primary beam to be focused to sub-50 nm for Cs$^+$ primary ions and sub-150 nm for O$^-$ primary ions. The trick is to get the secondary ions out efficiently and for that one uses the same lens analogous to a confocal light microscope in nano SIMS. By using primary and secondary beams of opposite charge, e.g. Cs$^+$ in, negative ions out, the two beams are separated by electrostatic deflection. The co-axial optics has a shorter working distance, smaller probe size, higher collection efficiency and minimization of shadowing effects. The main disadvantages with this technique are that the primary and secondary ions must be of opposite polarity and equal energy. This constraint means that minimization of matrix effects is not possible and oxygen flooding cannot be used. In a coaxial optic system, the secondary ions are extracted back through the primary ion beam diaphragm which controls lateral resolution but limits transmission and thereby sensitivity at the same time.

Figure 14 shows the behavior of cracks in 304 type stainless steel samples (34). A Cs$^+$ primary beam, focused to less than 50 nm, was used to sputter negative secondary ions from the sample surface. These ions were mapped on five detectors simultaneously. Nano SIMS maps from a crack tip are shown. The resolution is sufficient to separate the iron oxide (magnetite) (Fig. 14(a)) from the chromium oxide (Fig. 14(b)). Boron enrichment at the interface between the oxide and the fresh boundary (Fig. 14(c)) and boron segregated to the grain boundary (Fig. 14(d)) are clearly visible.

![NanoSIMS maps of a crack in 304 stainless steel. The boron map is shown twice at different intensities to reveal the enrichment at crack tip (c) and grain boundary segregation (d). After Lozano-Perez (34).](image)

**Atom Probe Field Ion Microscopy and Tomography**

Atom probe field-ion microscopy and atom probe tomography (35-36) have become one of the more powerful microanalytical techniques for the characterization of materials (37-38). The three-dimensional atom probes enable the position and the identity of millions of atoms obtained from a sample of the material to be reconstructed and analyzed.
with near atomic precision. The ability to determine the precise location of atoms in a material is one of the critical steps in designing new materials and structures. The atom probe traces its origins to the original field ion microscope invented in 1951 by Müller at Pennsylvania State University (39). In 1955, Bahadur and Müller obtained the first images of individual tungsten atoms in a field ion microscope.

In the field ion microscope, illustrated in Fig. 15(a), a sharp needle in Fig. 15(b), is mounted on a cryogenically cooled stage \( (T \approx 15-110 \text{ K}) \) in an ultra-high vacuum system (40). The needle should have a cylindrical cross section, an end radius of less than \(~50 \text{ nm}\), and a taper angle of \(<10^\circ\). Since the radius of the apex of the specimen increases during the experiment due to the continual removal of atoms from the surface, it is important to produce a needle with a starting end radius of \(~50 \text{ nm}\) or less and a high quality surface finish with no protrusions. The cylindrical symmetry is especially important in the 3-D atom probe, as the magnification and thus the lateral \( x \) and \( y \) distances are dependent on the local radius. A trace, \(~10^{-5} \text{ mbar}\), of helium or neon gas is introduced into the system. For a sufficiently high electric field, \(~30–50 \text{ V/nm}\), the gas atoms on the surface are field ionized by an electron tunneling process. As soon as the atoms at the tip become positively charged ions, they are repelled from the positively-charged specimen towards the phosphor screen. Upon impacting the phosphor screen they produce a spot of light. This process occurs across the entire surface of the needle, and the resulting pattern on the phosphor screen is the field ion image. By increasing the electric field on the specimen, the surface atoms are field ionized and evaporate from the specimen. The ion charge/mass, analyzed by a time-of-flight mass spectrometer, and the spatial location of each ion gives the chemical identity of each atom. One can resolve the chemical identity and position of individual atoms in 3-D with atomic resolution in the \( z \) direction and sub-nm lateral resolution. To measure the time of departure of the ion, the voltage is pulsed. The numbers of atoms of various elements that hit the detector are recorded and a mass spectrum is determined. The required high electric field necessitates the use of needle-shaped specimen.

The location of the atom in the specimen is determined from the ion's hit position on the detector. Since neither potential lines nor atomic flight paths can intersect or cross each other, an ion that hits the detector to the right of another ion must have been located to its right on the specimen. The depth, or \( z \) dimension, is provided by the sequence (time) of the ion hits on the detector. This process of field ionization provides a 3-D image of the entire specimen. Placing the detector at a distance from the specimen magni-

![Figure 15. (a) Schematic of the atom probe; (b) left: SEM image of an aluminum alloy tip; right microtip specimen of an Al/SiO$_2$/Si structure fabricated by broad ion beam milling. Cr was added to the structure as a control layer to aid in finding the original layers. Fig. 15(b) after Kelly and Miller (40).](image)
ties the tip of the specimen. The ions’ position in the plane parallel to the specimen surface can be calculated from the 2-D hit position of the ion on the detector with a lateral precision approaching 0.5 nm. Since atomic layers erode predictably from the specimen surface, sequence number can be used to calculate an ion’s position in the direction normal to the specimen surface in the original specimen with 0.2 nm resolution.

Historically, most atom probes have used voltage pulses to field evaporate atoms from the specimen. However, the specimen material must have electrical conductivity higher than about $10^2$ S/cm for the pulse to be effective, limiting the application of the voltage-pulsed atom probe primarily to conducting materials. For poorly conducting and insulating materials, femtosecond laser pulsing incident on atom probe specimen is rapidly becoming the preferred method of operation for atom probe tomography. Most of the methods developed for TEM specimen preparation can be directly applied to atom probe specimen preparation. The focused ion beam instrument is an excellent tool for sample preparation. Some instruments also combine a scanning electron microscope with the FIB column, enabling imaging of the sample, to ensure a good tip shape, and accurate positioning of the region of interest near the tip. With the high speed of data analysis available in today’s atom probes, specimen preparation has become the main bottleneck in the process.

In the local electrode atom probe (LEAP), a planar specimen contains many tips. By applying a high voltage between planar microtip specimen and a flat screen, the field at any one tip will not be high enough for field evaporation. A small aperture is scanned over the surface at high potential, shown in Fig. 16, until ions are extracted from one of the protrusions in the “scanning atom probe.” (41) The first commercial 3D atom probe was the position-sensitive atom probe of Cerezo et al. in 1988 (42). The instrument featured the same basic configuration of an imaging atom probe with the important distinction that the single-atom detector was able to encode the positions of the impacts of each ion. As a refinement of this instrument to minimize this multihit problem and for higher data collection rates, Kelly et al. proposed the wedge-and-strip anode with additional electrodes and segmentation of the detector into different subdetectors (43).

Though images are orders of magnitude larger now than a decade ago, the finite analyzed volume still limits the application of the atom probe. The largest field of view is about 200 nm today. This characteristic length scale can be increased through incremental improvements by a factor of 2 or so, but it will not reach a micron easily. Common image data sets are 100 nm in diameter by 100 nm in depth ($10^6 \text{ nm}^3$) with $10^2$–$10^8$ atoms. With the right specimen, image sizes of $10^9$ atoms are within reach. At today’s highest data collection rate of $10^8$ atoms/min it takes 17 h of data collection. 100 ppb sensitivity might be reached in such a specimen.

Figure 17-left shows a 3-D elemental map of Si, As, P, B, and O (44). To clarify the map of the dopants, only 5% of the atoms of Si atoms are shown. The MOSFET structure is seen (As and P atoms in the poly-Si gate and B atoms in the Si substrate). The As and P atoms in the poly-Si gate are not uniformly distributed. Figure 17-right shows a.
$^{28}$Si/$^{30}$Si isotope superlattice (SL) (45). These superlattices are composed of alternating layers of highly enriched $^{28}$Si and $^{30}$Si stable isotopes. Each isotopically enriched layer is only 1 nm thick. The mass difference between $^{28}$Si and $^{30}$Si is so small that it hardly affects the Si processing. Hence, the Si isotope SLs fulfill all the criteria imposed for atom probe microscopy standards. Alternating Si isotope layers are clearly observed along with the ~30 nm thick Ni cap and the natSi layer in the region deeper than ~80 nm. Figure 17-right(b) shows the enlargement of a middle part of the image of 17-right(a). Atomically flat interfaces of $^{28}$Si/$^{30}$Si appear concaved in Fig. 17-right(b). This artifact comes from the limitation in reconstructing images assuming that the atom emitting surface remains hemispherical through the measurement. Figure 17-right(c) shows the iso-concentration surface of the Si isotope SL in 3D.

![Figure 17](image.png)

Figure 17. Left: 3D elemental map of a MOSFET. As (yellow), P (red), B (white), O (blue), and Si (magenta), after ref. 46; right: A 3-D map of Si isotopes in the $^{28}$Si (1 nm)/$^{30}$Si(1 nm) isotope SL. The volume is 90 nm x 90 nm x 140 nm. A 30 nm thick Ni cap layer is at the top. Red, green, and blue dots represent $^{28}$Si, $^{30}$Si, and Ni atoms, respectively; (b) enlarged view of the part of (a) indicated in the figure. Only ~30% of the collected atoms is shown. (c) 3-D iso-concentration surface; after Shimizu et al. (45).

**X-Ray Characterization**

**X-Ray Tomography**

In X-ray tomography a series of projection images provide the data to calculate a three-dimensional reconstruction of an object. Contrast in transmission X-ray imaging is mainly based on absorption differences between different materials within the sample. It is used in the medical community for non invasive X-ray imaging of the human anatomy. The impact of this technique in diagnostic medicine has been revolutionary, since it has enabled doctors to view internal organs with unprecedented precision. The same technique is used for non-destructive inspections of parts and components with the object viewed in three dimensions using virtual cross sections of internal structures.

Conventional micro tomography has spatial resolution from a few microns to tens of microns - insufficient to observe defects in semiconductor devices. High-resolution X-ray microscopy or nanotomography is increasingly used in synchrotron radiation research to characterize biological, composites and nanomaterials. More recently, the development of the hard X-ray tomographic microscope uses the Cr-Kα emission line with spatial resolution of 60 nm, and more recently 8 keV Cu-Kα X-rays, enabling 3-D tomographic imaging of Cu interconnects through up to 30 µm thick IC silicon die (46).
Its application to high-resolution materials characterization had to await the implementation of X-ray focusing with zone plates, which are circular transmission gratings with radially increasing line density and use constructive interference of X-rays from adjacent zones to form a focus. The focal length of a zone plate is a function of its diameter, its outermost zone width and the X-ray wavelength. The numerical aperture, given by the maximum diffraction angle, is determined by the outermost zone. X-rays of 2.4 nm wavelength can resolve 25 nm feature size, approximately 10 times better than visible light microscopy (47).

![Figure 18. X-ray tomograph of a tungsten plug from 141 2-D images at 1° intervals. A 50-80 nm diameter void is seen in the 250x500 nm² plug. After Yin et al. (48).](image)

X-ray micro and nanotomography offers a powerful technique in non destructive characterization of package and die level defects respectively. Virtual delayering of reconstructed data offers a novel approach towards localization of failures in IC or packages without physical deprocessing. Figure 18 shows a tomographic image of a tungsten plug of an IC interconnect, obtained with X-rays of 0.118 nm wavelength. Such plugs are prone to failure through the formation of central voids during the deposition process. These X-rays are sufficiently energetic to pass through a silicon layer up to about 50 μm thick, ensuring an appropriately contrasted image. Two-dimensional images with incident X-ray angles from -70° to 70° in 1° increments were taken, with an exposure time of about a minute each (48).

The current 60-nm limit on spatial resolution is largely a result of the outer-zone width and thickness of the available zone plates, together with restrictions in the depth of field and the limited angular range in the data sets. Two-dimensional images resolved to 15 nm have been achieved in the soft X-ray region (49), albeit with a reduced depth of field. With hard X-rays, 30 nm spatial resolution in two dimensions has been achieved (50). Higher energy X-rays generally have the advantage of longer focal lengths, allowing a greater working distance. The disadvantage of hard X-rays is the need for thicker zone plates, which are more difficult to fabricate with the requisite narrow outer zones.

Summary

I have described several characterization techniques that have recently been developed for either lateral and/or vertical high-resolution measurements. High resolution is usually, but not always, in the nm or sub nm range. Mechanical probes, STM and AFM, have the ability to image and move individual atoms. Magnetic exchange force microscopy has extended AFM, when coupled with a magnetic field, into the 0.0015 nm vertical resolution range. Optical methods, based on interference, have sub-nm vertical resolution, although their lateral resolution, determined by the wavelength of the light, is modest. TEM, with third-order aberration correction, allows individual atoms to be displayed. Electron holography allows the potentials within semiconductor devices to be de-
termined. It is further used to determine lateral doping profiles and in failure analysis. SIMS through recent nano-SIMS is capable of 50 nm lateral resolution. Atom probe field ion microscopy, through appropriate sample preparation of sharply-pointed needles, displays the distribution of individual atoms within a matrix of other atoms. It has very high lateral and vertical resolution. X-ray tomography, routinely used for medical imaging to “look into” the body or head, through zone plate focusing is used to look into regions of a semiconductor device or interconnects.

No doubt we will continue to see further developments in these and other characterization techniques. Three-dimensional characterization of semiconductor devices at the near atomic level is increasingly important, especially for semiconductor logic and memory devices as well as quantum structured devices. Chemical resolution down to the ppm level is needed while maintaining sub-nm spatial resolution. Atom probe tomography is capable of these detection levels and will continue to make advances by using advanced FIB sample preparation. These are merely a few examples of future advances. Others will emerge as the need arises.

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References