

Rasterelektronenmikroskopie und Probenpräparation¹



Literatur:

R. F. Egerton, "Physical Principles of Electron Microscopy" (Springer, 2005)
A. A. Everwand, Bachelorarbeit, WWU (2015)
L. Reimer und H. Kohl, "Transmission Electron Microscopy" (Springer, 2008)
Ted Pella, Inc., Technical Notes - PELCO STEM Imaging Holder

Online-Zugriff:

<http://dx.doi.org/10.1007/b136495>
<https://www.uni-muenster.de/Physik.PI/Kohl/pub.html>
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https://www.tedpella.com/technote_html/16412_16412-4_TN.pdf

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Inhalt der Anleitung

Die Anleitung enthält keine Beschreibungen der Versuche, sondern es werden die theoretischen Grundlagen zum Verständnis der durchgeführten Versuche vermittelt. Ähnlich zu den Experimentellen Übungen 2 wird dabei auf vorhandene Literatur zurückgegriffen.

Möglicher Ablauf des Versuchs

Der Versuch ist aufgeteilt in zwei Versuchstage. Am ersten Versuchstag erfolgt zunächst eine Einarbeitung in das Hitachi S-4000 Rasterelektronenmikroskop (SEM). Hierzu sind diverse SEM-taugliche Proben vorhanden. Bei der Probenauswahl kann auf die Wünsche der Teilnehmer eingegangen werden. Insbesondere können auch von den Teilnehmern mitgebrachte Proben untersucht werden, falls sich diese als geeignet erweisen (d.h. nicht zu groß oder zu nichtleitend sind). Im Laufe des Tages wird mit dem Röntgendetektor des SEM gearbeitet, um die Zusammensetzung von unbekannten Proben zu untersuchen. Für den ersten Versuchstag ist vor allem der angefügte Auszug aus R.F. Egertons “Physical Principles of Electron Microscopy” relevant.

Am zweiten Versuchstag sollen Nanocluster zur Betrachtung mit dem Transmissionselektronenmikroskop (TEM) präpariert werden (Literatur: Auszug aus der Bachelorarbeit von A.A. Everwand). Das Ergebnis der Präparation kann daraufhin im TEM (Literatur: Auszug aus L. Reimers und H. Kohls “Transmission Electron Microscopy”) betrachtet werden. Mit Hilfe eines speziellen STEM-Halters (Literatur: Technical Notes - PELCO STEM Imaging Holder) wird außerdem versucht werden, die Nanocluster auch im SEM abzubilden.

Protokoll

Wir erwarten kein vollständiges Protokoll von euch, so wie es bisher bei den experimentellen Übungen üblich war. Stattdessen reicht ein kurzer Bericht aus. Das bedeutet, dass ihr nicht detailliert auf die theoretischen Grundlagen eingehen sollt. Beim Schreiben des Protokolls könnt ihr davon ausgehen, dass auch der Leser die euch zur Verfügung stehende Literatur kennt und ihr müsst sie deshalb nicht nochmal in eigenen Worten wiedergeben. Die Beschreibung der Versuchsdurchführung und eine kurze Erläuterung der erzielten Ergebnissen ist ausreichend.

Chapter 5

THE SCANNING ELECTRON MICROSCOPE

As we discussed in Chapter 1, the scanning electron microscope (SEM) was invented soon after the TEM but took longer to be developed into a practical tool for scientific research. As happened with the TEM, the spatial resolution of the instrument improved after magnetic lenses were substituted for electrostatic ones and after a stigmator was added to the lens column. Today, scanning electron microscopes outnumber transmission electron microscopes and are used in many fields, including medical and materials research, the semiconductor industry, and forensic-science laboratories.

Figure 1-15 (page 19) shows one example of a commercial high-resolution SEM. Although smaller (and generally less expensive) than a TEM, the SEM incorporates an electron-optical column that operates according to the principles already discussed in Chapter 2 and Chapter 3. Accordingly, our description will be shorter than for the TEM, as we can make use of many of the concepts introduced in these earlier chapters.

5.1 Operating Principle of the SEM

The electron source used in the SEM can be a tungsten filament, or else a LaB₆ or Schottky emitter, or a tungsten field-emission tip. Because the maximum accelerating voltage (typically 30 kV) is lower than for a TEM, the electron gun is smaller, requiring less insulation. Axially-symmetric magnetic lenses are used but they are also smaller than those employed in the TEM; for electrons of lower kinetic energy, the polepieces need not generate such a strong magnetic field. There are also *fewer* lenses; image formation uses the scanning principle that was outlined in Chapter 1, and as a result *imaging lenses* are not required.

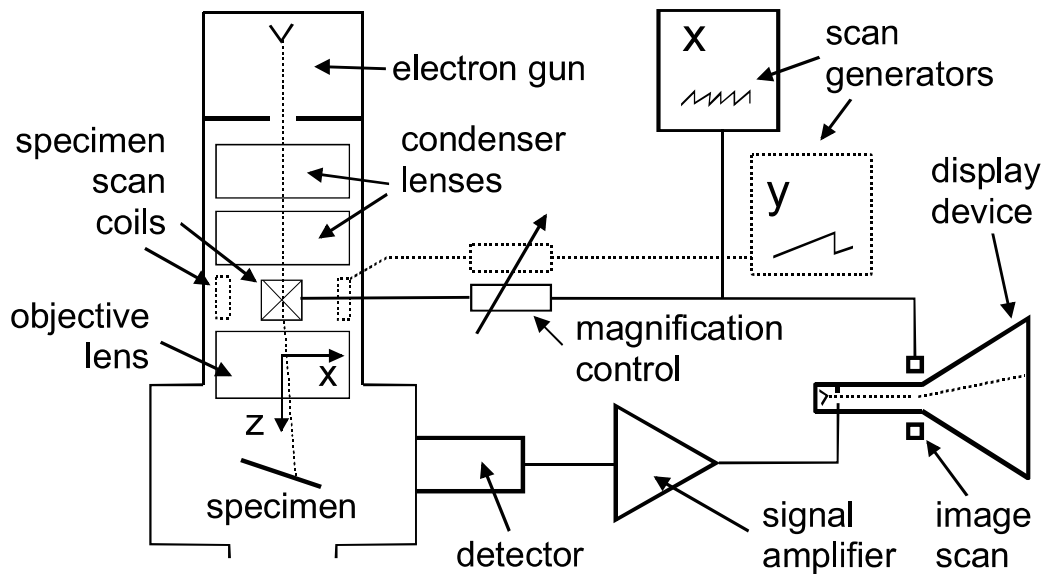


Figure 5-1. Schematic diagram of a scanning electron microscope with a CRT display.

Above the specimen, there are typically two or three lenses, which act somewhat like the condenser lenses of a TEM. But whereas the TEM, if operating in imaging mode, has a beam of diameter $\approx 1 \mu\text{m}$ or more at the specimen, the incident beam in the SEM (also known as the **electron probe**) needs to be as small as possible: a diameter of 10 nm is typical and 1 nm is possible with a field-emission source. The final lens that forms this very small probe is named the **objective**; its performance (including aberrations) largely determines the spatial resolution of the instrument, as does the objective of a TEM or a light-optical microscope. In fact, the resolution of an SEM can never be better than its incident-probe diameter, as a consequence of the method used to obtain the image.

Whereas the conventional TEM uses a stationary incident beam, the electron probe of an SEM is scanned horizontally across the specimen in two perpendicular (x and y) directions. The x -scan is relatively fast and is generated by a sawtooth-wave generator operating at a **line** frequency f_x ; see Fig. 5-2a. This generator supplies scanning current to two coils, connected in series and located on either side of the optic axis, just above the objective lens. The coils generate a magnetic field in the y -direction, creating a force on an electron (traveling in the z -direction) that deflects it in the x -direction; see Fig. 5-1.

The y -scan is much slower (Fig. 5-2b) and is generated by a second sawtooth-wave generator running at a **frame** frequency $f_y = f_x / n$ where n is an integer. The entire procedure is known as **raster scanning** and causes the beam to sequentially cover a rectangular area on the specimen (Fig. 5-2d).

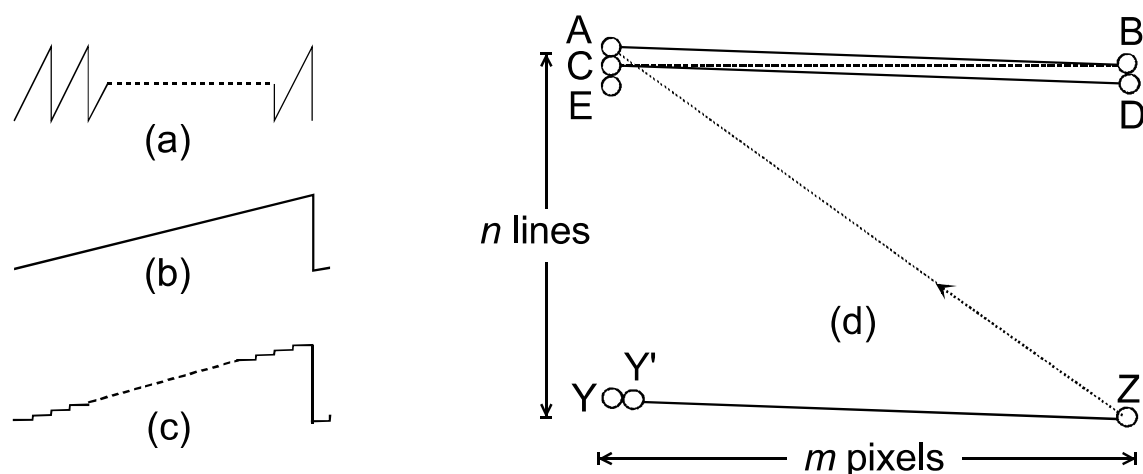


Figure 5-2. (a) Line-scan waveform (scan current versus time), (b) frame-scan waveform, and (c) its digital equivalent. (d) Elements of a single-frame raster scan: AB and YZ are the first and last line scans in the frame, Y and Y' represent adjacent pixels.

During its x -deflection signal, the electron probe moves in a straight line, from A to B in Fig. 5-2d, forming a single **line scan**. After reaching B, the beam is deflected back along the x -axis as quickly as possible (the **flyback** portion of the x -waveform). But because the y -scan generator has increased its output during the line-scan period, it returns *not* to A but to point C, displaced in the y -direction. A second line scan takes the probe to point D, at which point it flies back to E and the process is repeated until n lines have been scanned and the beam arrives at point Z. This entire sequence constitutes a single **frame** of the raster scan. From point Z, the probe quickly returns to A, as a result of the rapid flyback of *both* the line and frame generators, and the next frame is executed. This process may run continuously for many frames, as happens in TV or video technology.

The outputs of the two scan generators are also applied to a display device, such as a TV-type cathode-ray tube (CRT), on which the SEM image will appear. The electron beam in the CRT scans exactly in *synchronism* with the beam in the SEM, so for every point on the specimen (within the raster-scanned area) there is a *equivalent* point on the display screen, displayed at the same instant of time. Maxwell's first rule of imaging is therefore obeyed (although approximately because the electron beams are not points but circles of small diameter). In order to introduce *contrast* into the image, a voltage signal must be applied to the electron gun of the CRT, to vary the brightness of the scanning spot. This voltage is derived from a detector that responds to *some change in the specimen* induced by the SEM incident probe.

In a modern SEM, the scan signals are generated digitally, by computer-controlled circuitry, and the x - and y -scan waveforms are actually *staircase*

functions with m and n levels respectively; see Fig. 5-2c. This procedure divides the image into a total of mn picture elements (**pixels**) and the SEM probe remains stationary for a certain dwell time before *jumping* to the next pixel. One advantage of digital scanning is that the SEM computer “knows” the (x, y) address of each pixel and can record the appropriate image-intensity value (also as a digitized number) in the corresponding computer-memory location. A digital image, in the form of position and intensity information, can therefore be stored in computer memory, on a magnetic or optical disk, or transmitted over data lines such as the Internet.

Also, the modern SEM uses a flat-panel display screen in which there is no internal electron beam. Instead, computer-generated voltages are used to sequentially define the x - and y -coordinates of a screen pixel and the SEM detector signal is applied electronically to that pixel, to change its brightness. In other respects, the raster-scanning principle is the same as for a CRT display.

Image magnification in the SEM is achieved by making the x - and y -scan distances *on the specimen* a small fraction of the size of the displayed image, as by definition the magnification factor M is given by:

$$M = (\text{scan distance in the image}) / (\text{scan distance on the specimen}) \quad (5.1)$$

It is convenient to keep the image a *fixed* size, just filling the display screen, so increasing the magnification involves *reducing* the x - and y -scan currents, each in the same proportion (to avoid image distortion). Consequently, the SEM is actually working hardest (in terms of current drawn from the scan generator) when operated at *low* magnification.

The scanning is sometimes done at video rate (about 60 frames/second) to generate a rapidly-refreshed image that is useful for focusing the specimen or for viewing it at low magnification. At higher magnification, or when making a permanent record of an image, slow scanning (several seconds per frame) is preferred; the additional recording time results in a higher-quality image containing less electronic noise.

The signal that modulates (alters) the image brightness can be derived from any property of the specimen that changes in response to electron bombardment. Most commonly, the emission of **secondary electrons** (atomic electrons ejected from the specimen as a result of inelastic scattering) is used. However, a signal derived from **backscattered electrons** (incident electrons elastically scattered through more than 90 degrees) is also useful. In order to understand these (and other) possibilities, we need to

consider what happens when an electron beam enters a *thick* (often called bulk) specimen.

5.2 Penetration of Electrons into a Solid

When accelerated electrons enter a solid, they are scattered both *elastically* (by electrostatic interaction with atomic nuclei) and *inelastically* (by interaction with atomic electrons), as already discussed in Chapter 4. Most of this interaction is “forward” scattering, which implies deflection angles of less than 90° . But a small fraction of the primaries are elastically backscattered ($\theta > 90^\circ$) with only small fractional loss of energy. Due to their high kinetic energy, these backscattered electrons have a reasonable probability of leaving the specimen and re-entering the surrounding vacuum, in which case they can be collected as a backscattered-electron (**BSE**) signal.

Inelastic scattering involves relatively small scattering angles and so contributes little to the backscattered signal. However, it reduces the kinetic energy of the primary electrons until they are eventually brought to rest and absorbed into the solid; in a metal specimen they could become conduction electrons. The depth (below the surface) at which this occurs is called the **penetration depth** or the **electron range**. The volume of sample containing (most of) the scattered electrons is called the **interaction volume** and is often represented as pear-shaped in cross section (Fig. 5-3), because scattering causes the beam to spread laterally as the electrons penetrate the solid and gradually lose energy.

The electron range R for electrons of incident energy E_0 is given by the following approximate formula (Reimer 1998):

$$\rho R \approx a E_0^b \quad (5.2)$$

where $b \approx 1.35$ and ρ is the density of the specimen. If E_0 is given in *keV* in Eq. (5.2), $a \approx 10 \mu\text{g}/\text{cm}^2$. Expressing the range as a **mass-thickness** ρR makes the coefficient a roughly independent of atomic number Z . However, this implies that the distance R itself decreases with Z , as the densities of solids tend to increase with atomic number. For carbon ($Z = 6$), $\rho \approx 2 \text{ g}/\text{cm}^3$ and $R \approx 1 \mu\text{m}$ for a 10-keV electron. But for gold ($Z = 79$), $\rho \approx 20 \text{ g}/\text{cm}^3$ and $R \approx 0.2 \mu\text{m}$ at $E_0 = 10 \text{ keV}$. This strong Z -dependence arises mainly because backscattering depletes the number of electrons moving forward into the solid, the probability of such high-angle elastic scattering being proportional to Z^2 , as seen from Eq. (4.15). The interaction volume is therefore smaller for materials of higher atomic number (Fig. 5-3).

According to Eq. (5.2), the range decreases substantially with decreasing incident energy, not surprising because lower-energy electrons require fewer

inelastic collisions to bring them to rest and also the probability of inelastic scattering is inversely proportional to E_0 . A 1-keV electron penetrates only about 50 nm into carbon and less than 10 nm into gold. The interaction volume therefore becomes very small at low incident energy; see Fig. 5-3.

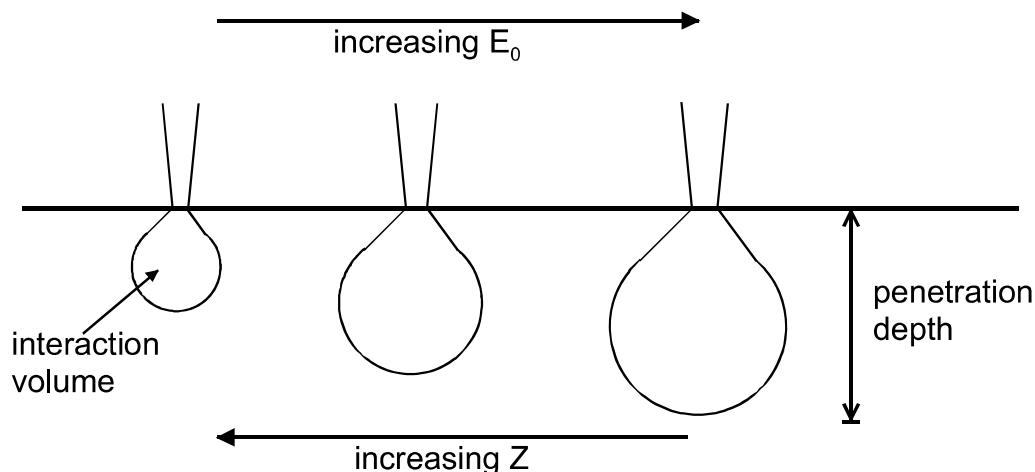


Figure 5-3. Schematic dependence of the interaction volume and penetration depth as a function of incident energy E_0 and atomic number Z of the incident (primary) electrons.

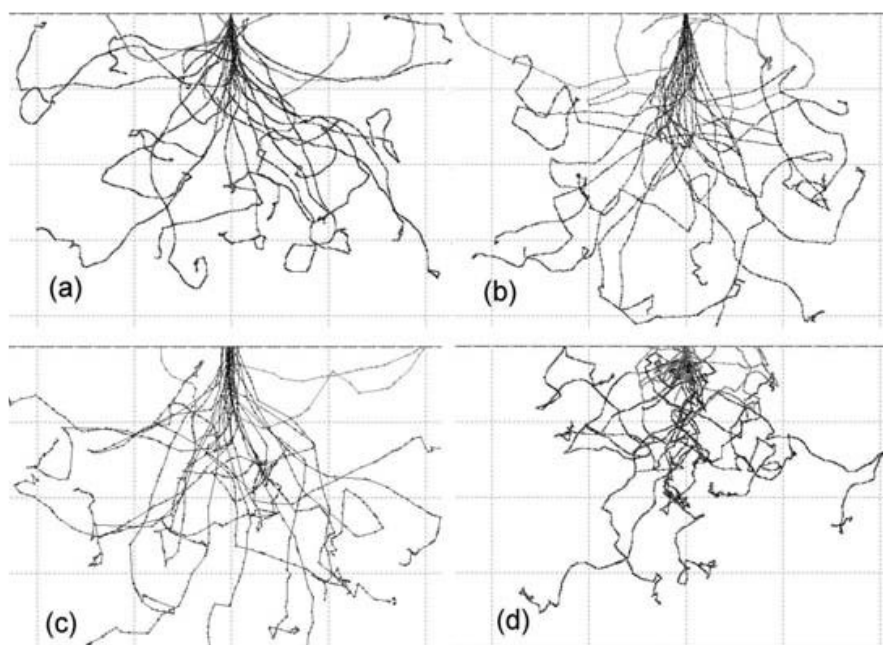


Figure 5-4. Penetration of (a) 30-keV, (b) 10-keV and (c) 3-keV electrons into aluminum ($Z = 13$) and (d) 30-keV electrons into gold ($Z = 79$). Note that the dimensional scales are different: the maximum penetration is about $6.4\ \mu\text{m}$, $0.8\ \mu\text{m}$, and $0.12\ \mu\text{m}$ in (a), (b), and (c), and $1.2\ \mu\text{m}$ in (d). These Monte Carlo simulations were carried out using the CASINO program (Gauvin et al., 2001) with 25 primary electrons and an incident-beam diameter equal to 10 nm in each case.

Penetration depth and interaction volume are macroscopic quantities, averaged over a large number of electrons, but the behavior of an *individual* electron is highly variable. In other words, scattering is a statistical process. It can be simulated in a computer by running a Monte Carlo program that contains a random-number generator and information about the angular distributions of elastic and inelastic scattering. Figure 5-4 shows the trajectories of 25 primary electrons entering both aluminum and gold. Sudden changes in direction represent the elastic or inelastic scattering. Although the behavior of each electron is different, the very dissimilar length scales needed to represent the different values of E_0 and Z in Fig. 5-4 are a further illustration of the overall trends represented by Eq. (5.2).

5.3 Secondary-Electron Images

From the principle of conservation of energy, we know that any energy *lost* by a primary electron will appear as a *gain* in energy of the atomic electrons that are responsible for the inelastic scattering. If these are the outer-shell (valence or conduction) electrons, weakly bound (electrostatically) to an atomic nucleus, only a small part of this acquired energy will be used up as potential energy, to release them from the confines of a particular atom. The remainder will be retained as kinetic energy, allowing the escaping electrons to travel through the solid as secondary electrons (abbreviated to **SE** or **secondaries**). As moving charged particles, the secondaries themselves will interact with other atomic electrons and be scattered inelastically, gradually losing their kinetic energy. In fact, most SEs start with a kinetic energy of less than 100 eV and, because the probability of inelastic scattering depends *inversely* on kinetic energy as in Eq. (4.16), the average distance that a secondary travels in the solid is very small, typically one or two nm.

As a result, most secondaries are brought to rest *within* the interaction volume. But those created close to the surface may escape into the vacuum, especially if they are initially traveling *toward* the surface. On average, the *escaping* secondaries are generated only within very small depth (< 2 nm) below the surface, called the **escape depth**. Because the SE signal used in the SEM is derived from secondaries that escape into the vacuum, the SE image is a property of the *surface structure* (topography) of the specimen rather than any underlying structure; the image is said to display **topographical contrast**.

The average number of *escaping* secondaries *per primary electron* is called the **secondary-electron yield**, δ , and is typically in the range from 0.1 to 10; the exact value depends on the chemical composition of the specimen

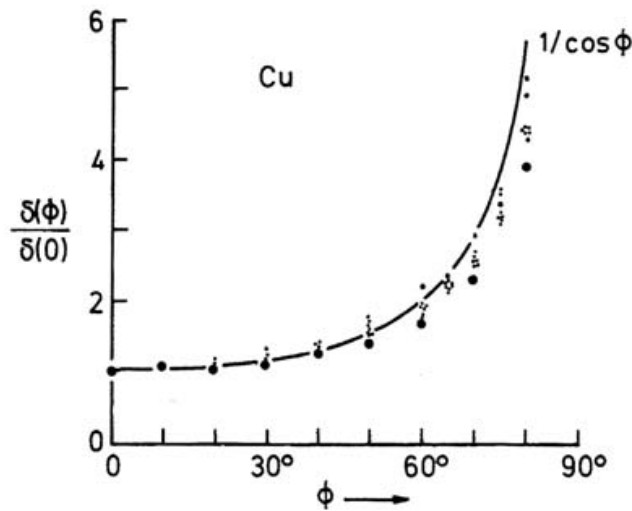


Figure 5-5. Dependence of SE yield on the angle of tilt ϕ of the specimen, measured between a plane perpendicular to its surface and the primary-electron beam ($\phi = 0$ corresponds to normal incidence). Data points represent experimental measurements and Monte Carlo predictions for copper; the curve represents a $1/\cos \phi$ function. From Reimer (1998), courtesy of Springer-Verlag.

(close to the surface) and on the primary-electron energy E_0 . For a given specimen, δ decreases with increasing E_0 because higher-energy primaries undergo less inelastic scattering (per unit distance traveled) and so there will be fewer secondaries generated *within the escape depth*.

As Fig. 5-5 indicates, the secondary-electron yield also depends on the angle between the incoming primary electron and the surface. The yield is lowest for normal (perpendicular) incidence and increases with increasing angle between the primary beam and the surface-normal. The reason is illustrated in Fig. 5-6a, which shows a focused nearly-parallel beam of primary electrons (diameter d) incident at two locations on a specimen, where the surface is normal (at A) and inclined (at B) to the incident beam. The region from which secondary electrons can escape is such that all points within it lie within the escape depth λ of the surface. For normal incidence, this escape region is a cylinder of radius $d/2$, height λ , and volume $V(0) = (\pi/4)d^2\lambda$. For the inclined surface, the escape region is a slanted cylinder with height λ (perpendicular to the surface) and base of cross-sectional area $(\pi/4)(d/\cos \phi)^2$, giving escape volume $V(\phi) = \pi(d/2)^2(\lambda/\cos \phi) = V(0)/\cos \phi$. Because the SE yield is proportional to the number of SE generated within the escape region, δ is proportional to the escape volume, resulting in:

$$\delta(\phi) = \delta(0)/\cos \phi \quad (5.3)$$

Measurements of $\delta(\phi)$ support this inverse-cosine formula; see Fig. 5-5.

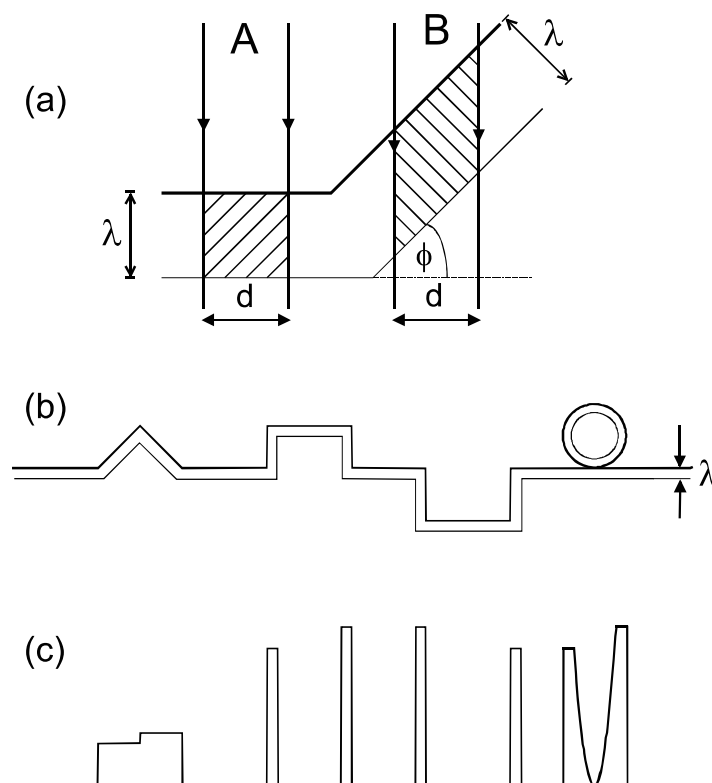


Figure 5-6. (a) SEM incident beam that is normal to a specimen surface (at A) and inclined to the surface (at B). The volume from which secondaries can escape is proportional to the shaded cross-sectional area, which is λd for case A and $\lambda d / \cos \phi$ for a tilted surface (case B). (b) Cross-sectional diagram of a specimen surface that contains triangular and square protrusions, a square-shaped trough or well, and a spherical particle; λ is the SE escape depth. (c) Corresponding secondary-electron signal (from a line-scan along the surface), assuming a SE detector that is located to the right of the specimen.

In qualitative terms, non-normal irradiation of a surface generates more SE that lie within a *perpendicular* distance λ of the surface and can therefore escape into the vacuum. For a surface with topographical (height) variations (Fig. 5-6b), this orientation dependence of δ results in protruding or recessed features appearing *bright in outline* in the SE image (Figs. 5-6c and 5-7a), similar to thickness-gradient contrast from a TEM replica.

In practice, there is usually some asymmetry due to the fact that the SE detector is located to one side of the column (Fig. 5-1) rather than directly above. Surface features that are tilted *toward* the detector appear especially bright because electrons emitted from these regions have a greater probability of reaching the detector; see Fig. 5-7a. This fact can be used to *distinguish* raised features and depressions in the surface of the specimen, as illustrated in Fig. 5-6c. As a result, the SE image has a three-dimensional appearance, similar to that of a rough surface obliquely illuminated by light, which makes the topographical contrast relatively easy to interpret; see also Fig. 5-9a.

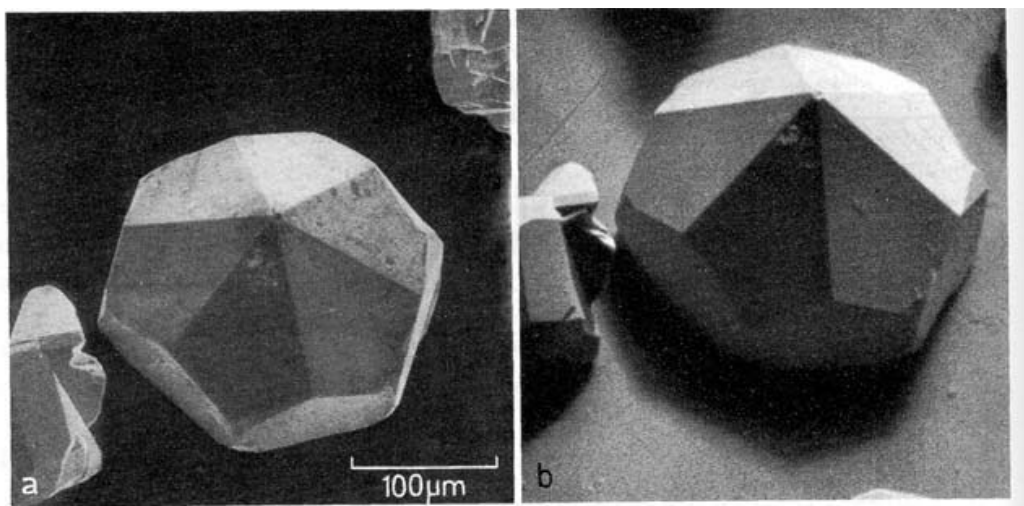


Figure 5-7. (a) Secondary-electron image of a small crystal; the side-mounted Everhart-Thornley detector is located toward the top of the image. (b) Backscattered-electron image recorded by the same side-mounted detector, which also shows topographical contrast and shadowing effects. Such contrast is much weaker for a BSE detector mounted directly above the specimen. From Reimer (1998), courtesy of Springer-Verlag.

Taking advantage of the orientation dependence of δ , the *whole sample* is often tilted away from a horizontal plane and toward the detector, as shown in Fig. 5-1. This increases the overall SE signal, averaged over all regions of the sample, while preserving the topographic contrast due to *differences* in surface orientation.

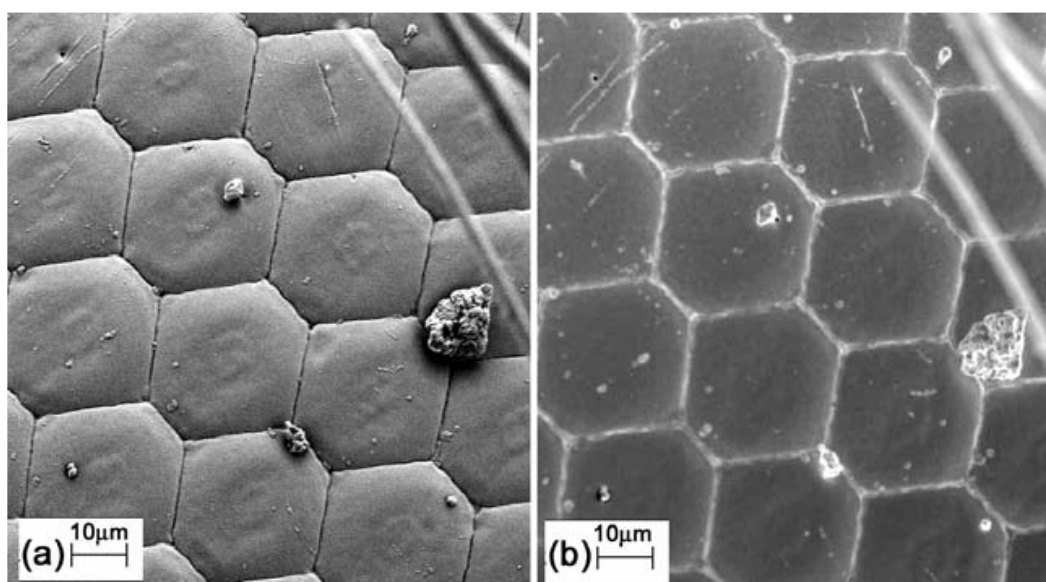


Figure 5-9. Compound eye of an insect, coated with gold to make the specimen conducting. (a) SE image recorded by a side-mounted detector (located toward the top of the page) and showing a strong directional effect, including dark shadows visible below each dust particle. (b) SE image recorded by an in-lens detector, showing topographical contrast but very little directional or shadowing effect. Courtesy of Peng Li, University of Alberta.

5.4 Backscattered-Electron Images

A backscattered electron (BSE) is a primary electron that has been ejected from a solid by scattering through an angle greater than 90 degrees. Such deflection could occur as a result of several collisions, some or all of which might involve a scattering angle of *less* than 90 degrees; however, a *single* elastic event with $\theta > 90$ degrees is quite probable. Because the elastic scattering involves only a *small* energy exchange, most BSEs escape from the sample with energies not too far below the primary-beam energy; see Fig. 5-10. The secondary and backscattered electrons can therefore be distinguished on the basis of their kinetic energy.

Because the cross section for high-angle elastic scattering is proportional to Z^2 , we might expect to obtain strong *atomic-number* contrast by using backscattered electrons as the signal used to modulate the SEM-image intensity. In practice, the **backscattering coefficient** η (the fraction of primary electrons that escape as BSE) *does* increase with atomic number, (almost linearly for low Z), and BSE images can show contrast due to variations in chemical composition of a specimen, whereas SE images reflect mainly its surface topography.

Another difference between the two kinds of image is the *depth* from which the information originates. In the case of a BSE image, the signal comes from a depth of up to about *half* the penetration depth (after being generated, each BSE must have enough energy to get out of the solid). For primary energies above 3 kV, this means some *tens or hundreds* of nanometers rather than the much smaller SE escape depth (≈ 1 nm).

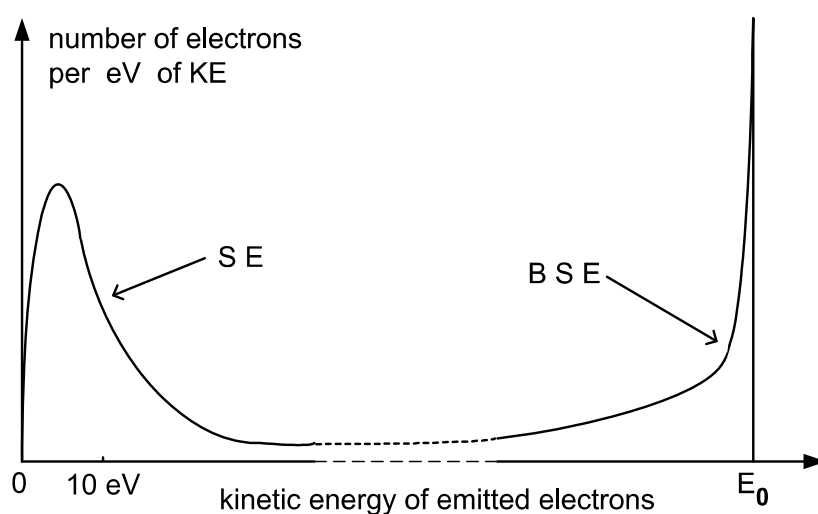


Figure 5-10. Number of electrons emitted from the SEM specimen as a function of their kinetic energy, illustrating the conventional classification into secondary and backscattered components.

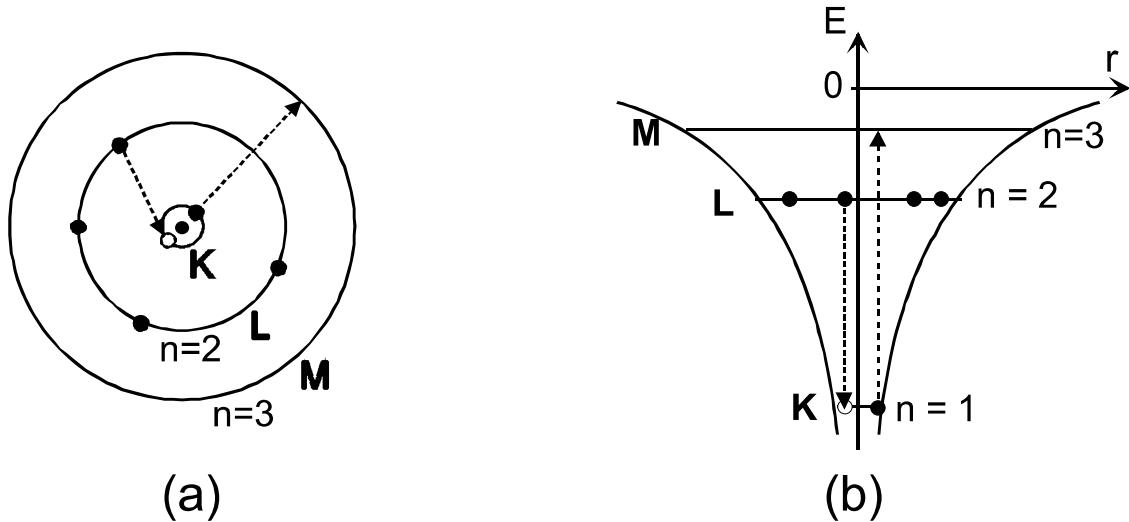


Figure 6-1. Bohr model of a carbon atom, visualized in terms of (a) electron orbits and (b) the equivalent energy levels. The orbits are also described as electron shells and are designated as K ($n = 1$), L ($n = 2$), M ($n = 3$) and so forth. The dashed arrows illustrate a possible scenario for x-ray emission: a K-shell electron ($n_l = 1$) is excited to the empty M-shell ($n_u = 3$) and an L-shell electron fills the K-shell vacancy in a de-excitation process ($n_l = 1$, $n_u = 2$).

$$hf = -R Z^2/n_u^2 - (-R Z^2/n_l^2) = R Z^2(1/n_l^2 - 1/n_u^2) \quad (6.5)$$

6.2 X-ray Emission Spectroscopy

When a primary electron enters a TEM or SEM specimen, it has a (small) probability of being scattered inelastically by an *inner-shell* (e.g. K-shell) electron, causing the latter to undergo a transition to a higher-energy orbit (or wave-mechanical state) and leaving the atom with an electron vacancy (hole) in its inner shell. However, the scattering atom remains in this *excited* state for only a very brief period of time: within about 10^{-15} s, one of the other atomic electrons fills the inner-shell vacancy by making a *downward* transition from a higher energy level, as in Fig. 6-1b. In this de-excitation process, energy can be released in the form of a *photon* whose energy (hf) is given roughly by Eq. (6.5) but more accurately by the *actual* difference in binding energy between the upper and lower levels.

The energy of this **characteristic x-ray** photon therefore depends on the atomic number Z of the atom involved and on the quantum numbers (n_l , n_u) of the energy levels involved in the electron transition. Characteristic x-rays can be classified according to the following historical scheme. The electron shell in which the original inner-shell vacancy was created, which corresponds to the quantum number n_l , is represented by an upper-case

letter; thus K implies that $n_l = 1$, L implies $n_l = 1$, M implies $n_l = 1$ and so on. This Roman symbol is followed by a Greek letter that represents the *change in* quantum number: α denotes $(n_u - n_l) = 1$, β denotes $(n_u - n_l) = 2$, and γ denotes $(n_u - n_l) = 3$. Sometimes a numerical subscript is added to allow for the fact that some energy levels are split into components of slightly different energy, due to quantum-mechanical effects.

The transition sequence represented in Fig. 6-1b would therefore result in a $K\alpha$ x-ray being emitted, and in the case of carbon there is no other possibility. With an atom of higher atomic number, containing electrons in its M-shell, an M- to K-shell transition would result in a $K\beta$ x-ray (of greater energy) being emitted. Similarly, a vacancy created (by inelastic scattering of a primary electron) in the L-shell might result in emission of an $L\alpha$ photon. These possibilities are illustrated in Fig. 6-2, which shows the x-ray emission spectrum recorded from a TEM specimen consisting of a thin film of nickel oxide (NiO) deposited onto a thin carbon film and supported on a molybdenum (Mo) TEM grid.

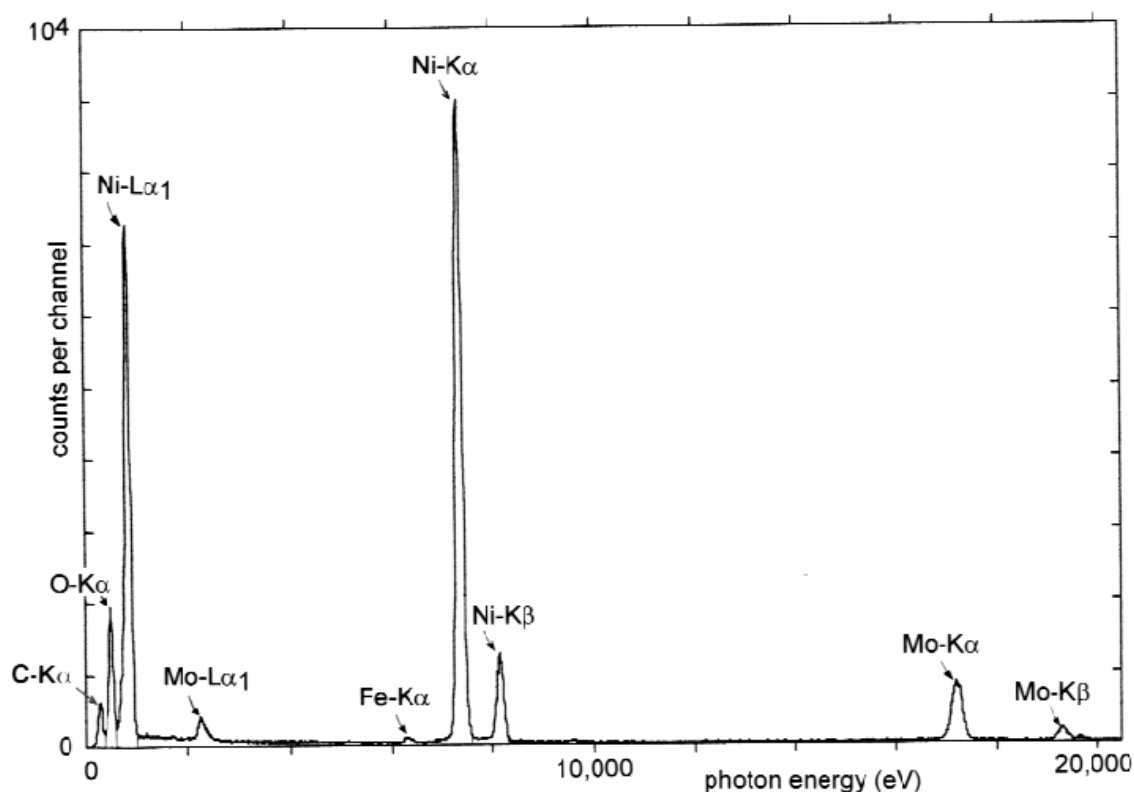


Figure 6-2. X-ray emission spectrum (number of x-ray photons as a function of photon energy) recorded from a TEM specimen (NiO thin film on a Mo grid), showing characteristic peaks due to the elements C, O, Ni, Mo, and Fe. For Ni and Mo, both K- and L-peaks are visible. Mo peaks arise from the grid material; the weak Fe peak is from the TEM polepieces.

Figure 6-2 also demonstrates some general features of x-ray emission spectroscopy. First, each element gives rise to *at least one* characteristic peak and can be identified from the photon energy associated with this peak. Second, medium- and high-Z elements show *several* peaks (K, L, etc.); this complicates the spectrum but can be useful for multi-element specimens where some characteristic peaks may overlap with each other, making the measurement of elemental concentrations problematical if based on only a single peak per element. Third, there are always a few stray electrons outside the focused electron probe (due to spherical aberration, for example), so the x-ray spectrum contains contributions from elements in the nearby environment, such as the TEM support grid or objective-lens polepieces.

High-Z atoms contain a large number of electron shells and can in principle give rise to *many* characteristic peaks. In practice, the number is reduced by the need to satisfy conservation of energy. As an example, gold ($Z = 79$) has its K-emission peaks above 77 keV, so in an SEM, where the primary-electron energy is rarely above 30 keV, the primary electrons do not have enough energy to excite K-peaks in the x-ray spectrum.

The characteristic peaks in the x-ray emission spectrum are superimposed on a continuous background that arises from the **bremsstrahlung** process (German for braking radiation, implying deceleration of the electron). If a primary electron passes close to an atomic nucleus, it is elastically scattered and follows a curved (hyperbolic) trajectory, as discussed in Chapter 4. During its deflection, the electron experiences a Coulomb force and a resulting centripetal acceleration toward the nucleus. Being a charged particle, it must emit electromagnetic radiation, with an amount of energy that depends on the impact parameter of the electron. The latter is a *continuous* variable, slightly different for each primary electron, so the photons emitted have a broad range of energy and form a background to the characteristic peaks in the x-ray emission spectrum. In Fig. 6-2, this bremsstrahlung background is low but is visible between the characteristic peaks at low photon energies.

Either a TEM or an SEM can be used as the means of generating an x-ray emission spectrum from a small region of a specimen. The SEM uses a thick (bulk) specimen, into which the electrons may penetrate several micrometers (at an accelerating voltage of 30 kV), so the x-ray intensity is higher than that obtained from the thin specimen used in a TEM. In both kinds of instrument, the volume of specimen emitting x-rays depends on the *diameter* of the primary beam, which can be made very small by focusing the beam into a probe of diameter 10 nm or less. In the case of the TEM, where the sample is thin and lateral spread of the beam (due to elastic scattering) is limited, the analyzed volume can be as small as 10^{-19} cm^2 , allowing detection

of less than 10^{-19} g of an element. In the SEM, x-rays are emitted from the entire interaction volume, which becomes larger as the incident energy of the electrons is increased (Fig. 5-3).

To generate a spectrum from the emitted x-rays, we need some form of *dispersive* device that distinguishes x-ray photons on the basis of either their energy ($E = hf$, where f is the frequency of the electromagnetic wave) or their wavelength ($\lambda = c/f = hc/E$, where c is the speed of light in vacuum). Although photon energy and wavelength are closely related, these two options give rise to two distinct forms of spectroscopy, which we discuss in Sections 6.3 and 6.6.

6.3 X-ray Energy-Dispersive Spectroscopy

In x-ray energy-dispersive spectroscopy (XEDS), the dispersive device is a semiconductor diode, fabricated from a single crystal of silicon (or germanium) and somewhat similar to the BSE detector in an SEM. If an x-ray photon enters and penetrates to the transition region (between p- and n-doped material), its energy can release a considerable number of outer-shell (valence) electrons from the confinement of a particular atomic nucleus. This process is equivalent to exciting electrons from the valence to the conduction band (i.e., the creation of electron-hole pairs) and results in electrical conduction by both electrons and holes for a brief period of time. With a reverse-bias voltage applied to the diode, this conduction causes electrical charge to flow through the junction (and around an external circuit), the charge being proportional to the number N of electron-hole pairs generated. Assuming that all of the photon energy (hf) goes into creating electron-hole (e-h) pairs, each pair requiring an average energy ΔE , energy conservation implies:

$$N = hf / \Delta E \quad (6.6)$$

For silicon, $\Delta E \approx 4$ eV (just over *twice* the energy gap between valence and conduction bands), therefore a Cu-K α photon creates about $(8000\text{eV})/(4\text{eV}) = 2000$ e-h pairs.

To ensure that essentially *all* of the incoming x-rays are absorbed and generate current pulses in an external circuit, the p-n transition region is made much *wider* than in most semiconductor diodes. In the case of silicon, this can be done by diffusing in the element lithium ($Z = 3$), which annihilates the effect of other electrically-active (dopant) impurities and creates a high-resistivity (intrinsic) region several mm in width; see Fig. 6-3.

If the semiconductor diode were operated at room temperature, *thermal* generation of electron-hole pairs would contribute too much electronic noise

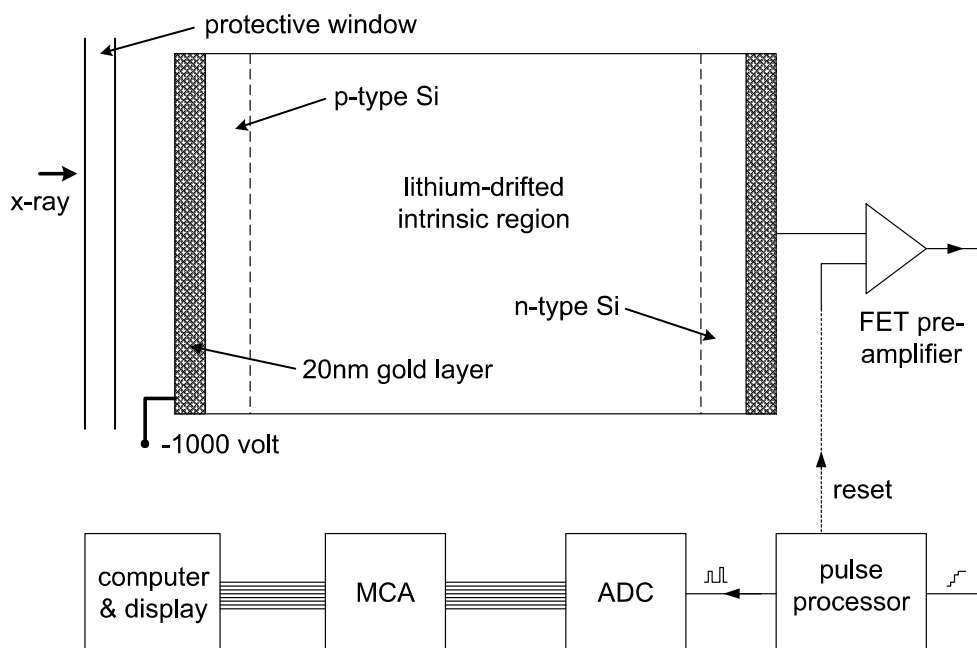


Figure 6-3. Schematic diagram of a XEDS detector and its signal-processing circuitry.

to the x-ray spectrum. Therefore the diode is cooled to about 140 K, via a metal rod that has good thermal contact with an insulated (dewar) vessel containing liquid nitrogen at 77 K. To prevent water vapor and hydrocarbon molecules (present at low concentration in an SEM or TEM vacuum) from condensing onto the cooled diode, a thin protective window precedes the diode; see Fig. 6-3. Originally this window was a thin ($\approx 8 \mu\text{m}$) layer of beryllium, which because of its low atomic number ($Z = 4$) transmits most x-rays without absorption. More recently, ultra-thin windows (also of low- Z materials, such as diamond or boron nitride) are used to minimize the absorption of low-energy ($< 1 \text{ keV}$) photons and allow the XEDS system to analyze elements of low atomic number ($Z < 12$) via their K-emission peaks.

The current pulses from the detector crystal are fed into a field-effect transistor (FET) preamplifier located just behind the diode (see Fig. 6-3) and also cooled to reduce electronic noise. For noise-related reasons, the FET acts as a *charge-integrating* amplifier: for each photon absorbed, its output voltage increases by an amount that is proportional to its input, which is proportional to N and, according to Eq. (6.6), to the photon energy. The output of the FET is therefore a *staircase* waveform (Fig. 6-4a) with the height of each step proportional to the corresponding photon energy. Before the FET output reaches its saturation level (above which the FET would no longer respond to its input), the voltage is reset to zero by applying an electrical (or optical) trigger signal to the FET.

A pulse-processing circuit (Fig. 6-3) converts each voltage step into a signal *pulse* whose height is proportional to the voltage step and which is therefore proportional to the photon energy; see Fig. 6-4b. An analog-to-digital converter (ADC) then produces a sequence of constant-height pulses from each signal pulse (Fig. 6-4c), their number being proportional to the input-pulse height. This procedure is called **pulse-height analysis (PHA)** and is also used in particle-physics instrumentation. Finally, a **multichannel analyzer (MCA)** circuit counts the number (n) of pulses in each ADC-output sequence and increments (by one count) the number stored at the n 'th location (address) of a computer-memory bank, signifying the recording of a photon whose energy is proportional to n , and therefore to N and to photon energy. At frequent time intervals (such as 1 s), the computer-memory contents are read out as a spectrum display (Fig. 6-4d) in which the horizontal axis represents photon energy and the vertical scale represents the number of photons counted at that energy.

Typically, the spectrum contains $2^{12} = 4096$ memory locations (known as channels) and each channel corresponds to a 10 eV range of photon energy, in which case the entire spectrum extends from zero and just over 40 keV, sufficient to include almost all the characteristic x-rays. Because the number N of electron-hole pairs produced in the detector is subject to a statistical variation, each characteristic peak has a width of *several* channels. The peaks therefore appear to have a smooth (Gaussian) profile, centered around the characteristic photon energy but with a width of ≈ 150 eV, as in Fig. 6-2.

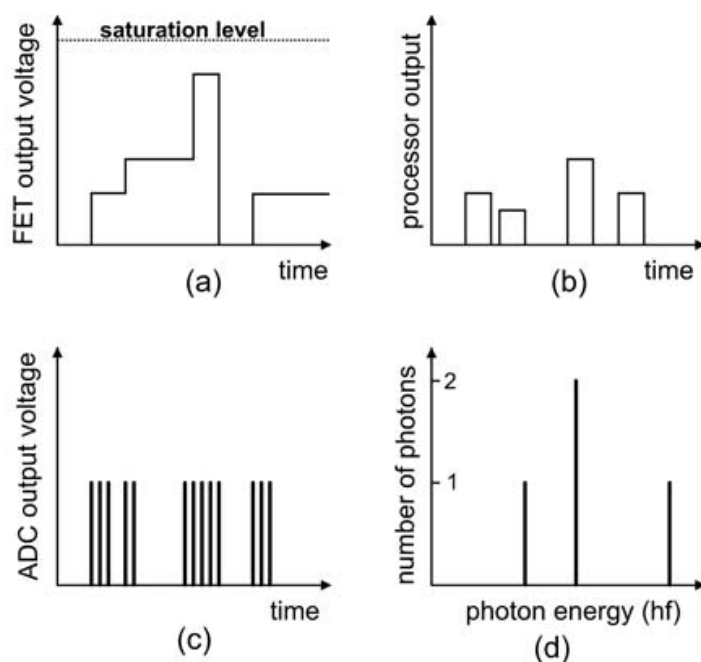


Figure 6-4. Voltage output signals of (a) the FET preamplifier, (b) the pulse-processor circuit, and (c) the analog-to-digital converter (ADC), resulting in (d) the XEDS-spectrum display.

Ideally, each peak in the XEDS spectrum represents an element present *within a known region of the specimen*, defined by the focused probe. In practice, there are often additional peaks due to elements beyond that region or even outside the specimen. Electrons that are backscattered (or in a TEM, forward-scattered through a large angle) strike objects (lens polepieces, parts of the specimen holder) in the immediate vicinity of the specimen and generate x-rays that are characteristic of those objects. Fe and Cu peaks can be produced in this way. In the case of the TEM, a special “analytical” specimen holder is used whose tip (surrounding the specimen) is made from beryllium ($Z = 4$), which generates a single K-emission peak at an energy below what is detectable by most XEDS systems. Also, the TEM objective aperture is usually removed during x-ray spectroscopy, to avoid generating backscattered electrons at the aperture, which would bombard the specimen from below and produce x-rays far from the focused probe. Even so, spurious peaks sometimes appear, generated from thick regions at the edge of a thinned specimen or by a specimen-support grid. Therefore, caution has to be used in interpreting the significance of the x-ray peaks.

It takes a certain period of time (conversion time) for the PHA circuitry to analyze the height of each pulse. Because x-ray photons enter the detector at random times, there is a certain probability of another x-ray photon arriving within this conversion time. To avoid generating a false reading, the PHA circuit ignores such double events, whose occurrence increases as the photon-arrival rate increases. A given recording time therefore consists of two components: **live time**, during which the system is processing data, and **dead time**, during which the circuitry is made inactive. The beam current in the TEM or SEM should be kept low enough to ensure that the dead time is less than the live time, otherwise the number of photons *measured* in a given recording time starts to fall; see Fig. 6-5.

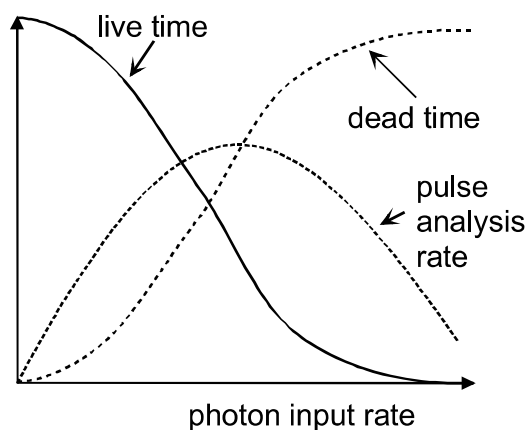


Figure 6-5. Live time, dead time, and pulse-analysis rate, as a function of the generation rate of x-rays in the specimen.

The time taken to record a useful XEDS spectrum is dictated by the need to clearly identify the *position* of each significant peak (its characteristic energy) and also, for measurement of elemental ratios, the *total number of photon counts* in each peak (the peak integral or area). If the recording time is too short, an insufficient number of x-ray photons will be analyzed and the spectrum will be “noisy.” This electronic noise arises from the fact that the generation of x-rays in the specimen is a statistical process, giving rise to a statistical variation in the number of counts per channel in the XEDS spectrum. According to the rules of (Poisson) statistics, if N randomly-arriving photons are recorded, we can expect a *variation* in that number (the standard deviation) equal to $N^{1/2}$ if the experiment were repeated many times. The accuracy of measuring N is therefore $N^{1/2}$ and the fractional accuracy is $N^{1/2}/N = N^{-1/2} = 0.1$ for $N = 100$. As a result, we need *at least* 100 x-ray counts in a characteristic peak in order to measure the concentration of the corresponding element to an accuracy of 10%. Typically, this condition implies a recording time of at least 10 s, and sometimes several minutes if the x-ray generation rate is low (e.g., with a thin specimen in the TEM).

One important feature of XEDS analysis is that it can provide a *quantitative* estimate of the concentration ratios of elements present in a specimen. The first requirement is to determine the number of characteristic x-ray photons contributing to each peak, by measuring the area (integral) of the peak and subtracting a contribution from the bremsstrahlung background. This background contribution is estimated by measuring the background on either side of the peak, then interpolating or (for greater accuracy) fitting the background to some simple mathematical function. However, the ratio of two peak integrals is *not* equal to the ratio of the elemental concentrations, as x-rays are not emitted with equal efficiency by different elements. The physics of x-ray production is simplest for the case of a very *thin* specimen, as used in the TEM, so we consider this situation first.

6.4 Quantitative Analysis in the TEM

For quantification, we need an equation that relates the number N_A of x-ray photons contributing to a characteristic peak of an element A to its concentration n_A (number of atoms of element A per unit volume). We can expect N_A to be proportional to the number N_e of electrons that pass through the sample during the XEDS recording time, and to the product $n_A t$, where t is the specimen thickness (for thin specimens, the probability of inner-shell inelastic scattering increases proportional to t).

However, the product $n_A t$ (termed the areal density of the element) has dimensions of m^{-2} , whereas N_A and N_e are dimensionless numbers. In order

to balance the units in our equation, there must be an additional factor whose dimensions are m^2 . This factor is the **ionization cross section** σ_A for creating a vacancy in an *inner shell* of element A. Such a cross section can be interpreted as a *target area* for inelastic scattering of an incident electron by the atom, as discussed Section 4.3. The value of σ_A depends on the type of inner shell (K, L, etc.) as well as on the atomic number of the element.

Still missing from our equation is a factor known as the **fluorescence yield** that allows for the fact that not *every* inner-shell vacancy gives rise to the emission of an x-ray photon during the de-excitation of the atom. An alternative process allows the excited atom to return to its ground state by donating energy to another electron within the atom, which is ejected as an **Auger electron** (named after its discoverer, Pierre Auger). For elements of low atomic number, this Auger process is the more probable outcome and their *x-ray* fluorescence yield ω is considerably less than one ($\omega \ll 1.0$).

A remaining factor, known as the **collection efficiency**, η , of the XEDS detector, reflects the fact that x-ray photons are emitted equally in all directions; they travel in straight-line paths and only a fraction η of them reach the detector. Combining all of these factors, the number of x-ray photons contributing to the characteristic peak of an element A is

$$N_A = (n_A t) \sigma_A \omega_A \eta N_e \quad (6.7)$$

Applying the same considerations to some other element B present in the sample, we could generate a second equation, identical to Eq. (6.7) but with subscripts B. Dividing Eq. (6.7) by this second equation, we obtain an expression for the *concentration ratio* of the two elements:

$$n_A/n_B = [(\sigma_B \omega_B)/(\sigma_A \omega_A)] (N_A/N_B) \quad (6.8)$$

The coefficient in square brackets is known as the **k-factor** of element A relative to element B. Although it is possible to *calculate* this *k*-factor from tabulated ionization cross sections and fluorescence yields, a more accurate value is obtained by *measuring* the peak-intensity ratio (N_A/N_B) in a spectrum recorded from a “standard” sample (such as a binary compound) whose concentration ratio (n_A/n_B) is known. This measured *k*-factor will also include any difference in collection efficiency between element A and element B (due to different absorption of x-rays in the detector window, for example).

The use of standards is common in analytical chemistry. But because the *k*-factor method was developed by metallurgists, the concentration ratio in Eq. (6.8) usually represents a *weight* ratio of two elements, rather than the *atomic* ratio n_A/n_B , and *k*-factors reflect this convention. Such *k*-factors have been measured and tabulated for most elements but their precise values

depend on the electron energy and detector design, so they are best measured using the *same* TEM/XEDS system as used for microanalysis. By analyzing characteristic peaks in pairs, the ratios of all elements in a multi-element specimen can be obtained from the measured peak integrals, knowing the appropriate *k*-factors. For further details, see Williams and Carter (1996).

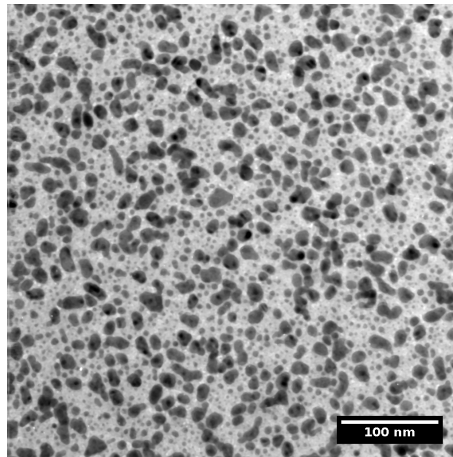
6.5 Quantitative Analysis in the SEM

In an SEM, electrons enter a thick specimen and penetrate a certain distance, which can exceed 1 μm (Section 5.2). Quantification is then complicated by the fact that many of the generated x-rays are absorbed before they leave the specimen. The amount of **absorption** depends on the *chemical composition* of the specimen, which is generally unknown (otherwise there is no need for microanalysis). However, x-ray absorption coefficients have been measured or calculated (as a function of photon energy) for all the chemical elements and are published in graphical or tabulated form. A legitimate procedure is therefore to *initially* assume *no* absorption of x-ray photons, by employing a procedure based on Eq. (6.8) to estimate the ratios of *all* of the elements in the specimen, then to use these ratios to estimate the x-ray absorption that *ought to* have occurred in the specimen. Correcting the measured intensities for absorption leads to a *revised* chemical composition, which can then be used to calculate absorption more accurately, and so on. After performing several cycles of this *iterative* procedure, the calculated elemental ratios should converge toward their true values.

Another complication is x-ray **fluorescence**, a process in which x-ray photons are absorbed but generate photons of lower energy. These lower-energy photons can contribute spurious intensity to a characteristic peak, changing the measured elemental ratio. Again, the effect can be calculated, but only if the chemical composition of the specimen is known. The solution is therefore to include fluorescence corrections, as well as absorption, in the iterative process described above. Because the ionization cross sections and yields are *Z*-dependent, the whole procedure is known as **ZAF correction** (making allowance for atomic number, absorption, and fluorescence) and is carried out by running a ZAF program on the computer that handles the acquisition and display of the x-ray emission spectrum.

Bachelorarbeit

Herstellung und Charakterisierung von Silber- und Goldnanoclustern



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1 Einführung

Nanopartikel sind für das bloße Auge nicht sichtbar und dennoch umgeben sie uns den ganzen Tag. Nicht nur, dass Nanopartikel sich in der Luft befinden, auch in alltäglichen Gegenständen sind Nanopartikel enthalten. So befinden sich Nanopartikel zum Beispiel in Reinigungsmitteln, in der Autoindustrie bei der Herstellung von Lacken finden sie Verwendung und im Bereich der Medizin werden sie zum Teil als Transportmittel für Medikamente eingesetzt. In dieser Arbeit wurde die Herstellung von Gold- und Silbernanoclustern in Edelgasatmosphäre in Bezug auf die Nanoclustergröße und deren Größenverteilung untersucht.

1.1 Nanocluster – Was ist das?

Bei einem Cluster handelt es sich um eine Gruppe von Atomen. Ein Nanocluster ist somit eine Gruppierung von Atomen in der Größenordnung 10^{-9} m, sie setzen sich aus wenigen Atomen (≈ 1000) zusammen und haben eine Größe von bis zu 100 nm. Nanocluster weisen wegen des geringen Volumens und der verhältnismäßig großen Oberfläche besondere chemische und physikalische Eigenschaften auf [1]. Aufgrund der hohen Oberflächenladung wegen des geringen Volumens haben sie eine hohe Stabilität. In der Chemie werden Nanopartikel als Katalysatoren genutzt, da sie aufgrund der großen Oberfläche im Verhältnis zum relativ kleinen Volumen eine höhere chemische Reaktivität haben. Man ist bestrebt, Katalysatoren in einer Größe von wenigen nm herzustellen.

1.2 Besondere Eigenschaften von Silber und Gold

In dieser Arbeit wurde die Herstellung und Charakterisierung von Nanoclustern aus Silber und Gold näher betrachtet [2]. Bei Silber und Gold handelt es sich jeweils um chemische Elemente der 1. Nebengruppe, sie gehören somit der Gruppe der Übergangsmetalle an. Liegen Silber und Gold in kristalliner Form vor, bilden sie eine kubisch-flächenzentrierte Struktur. Der Atomradius von Gold ist 135 pm und der kovalente Radius ist 144 pm. Der Siedepunkt liegt bei 2856 °C und die Verdampfungswärme ist 334,4 kJ/mol. Der Atomradius von Silber beträgt 160 pm und der kovalente Radius beträgt 153 pm. Der Siedepunkt von Silber liegt bei 2162 °C und die Verdampfungswärme ist 250,58 kJ/mol.

Aufgrund der chemischen Eigenschaften von Übergangsmetallen eignen sich die Materialien Silber und Gold sehr gut zur Herstellung von Katalysatoren. Der Vorteil des Einsetzens von Nanoclustern als Katalysatoren ist die große Oberfläche im Verhältnis zum Volumen.

Bei Silber handelt es sich um ein duktiles Schwermetall, welches eine große thermische Leitfähigkeit aufweist. Zudem hat Silber die größte elektrische Leitfähigkeit aller Elemente.

2 Herstellung der Nanocluster

Um die Herstellung von Nanoclustern näher zu untersuchen, wurden im Laufe dieser Arbeit ca. 80 Silberproben und 60 Goldproben hergestellt. Die Nanocluster wurden auf Kupfernetzen, die mit einer Kohlenstoffschicht versehen waren, aufgedampft und hinsichtlich Größe und Gleichmäßigkeit ausgewertet.

2.1 Kohlenstoffschicht als Träger für die Nanocluster

Im ersten Herstellungsschritt wurden die Probenträger (mit Kohlenstoff beschichtete Kupfernetze) hergestellt[5, Kap. 14.2.3 Kohleverdampfung], auf die im nächsten Herstellungsschritt die Gold- und Silbernanocluster aufgedampft wurden. Um eine homogene Trägerschicht herzustellen, wurde Kohlenstoff im Hochvakuum ($3 \cdot 10^{-5}$ mbar) verdampft. Es wurde hierzu an einen Graphitstab eine Spannung angelegt und soweit erhöht, bis er zu glühen begann. Durch weiteres Erhitzen ging der Kohlenstoff in den gasförmigen Zustand über und hat sich im Vakuum ausgebreitet und auf den Glasträgern sowie dem gesamten Inneren der Vakuumblocke abgesetzt. Es hat sich eine homogene Kohlenstoffschicht auf den Glasträgern gebildet, die anschließend in destilliertem Wasser von den Trägern gelöst und mit Cu-Netzen mit 400 Mesh (Mesh = Stege pro 25,4 mm) aufgenommen wurde. Nach einer Trocknungsphase (ca. 1 h) konnte mit dem Bedampfen der Probenträger begonnen werden.

2.2 Aufdampfungsprozess der Nanocluster

Die mit Kohlenstoff beschichteten Trägernetze hatten einen Durchmesser von 3,05 mm und wurden so in eine Halterung eingesetzt, dass die Kohlenstoffschicht zur Öffnung

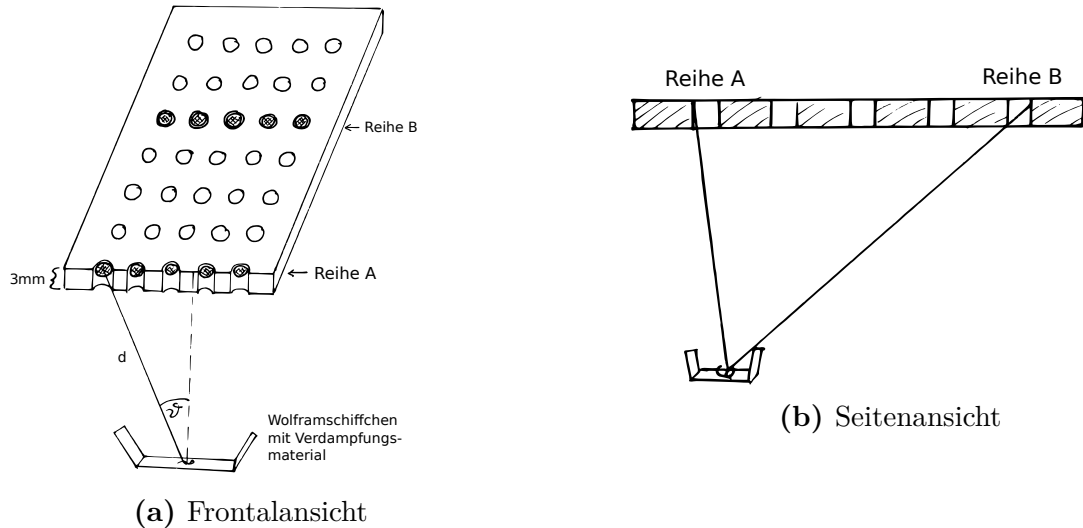


Abbildung 2.1: Verteilung der Netze in der Halterung beim Aufdampfen.

zeigte. Diese Halterung bestand aus einer Metallplatte ($(3,0 \pm 0,1)$ mm stark) mit Bohrungen (Durchmesser $(2,5 \pm 0,1)$ mm) in regelmäßigen Abständen. Der Abstand zwischen den einzelnen Bohrungen betrug $(5,5 \pm 0,1)$ mm. Pro Verdampfungsprozess wurden 10 Netze, wie in Abb. 2.1a zu sehen, in die Halterung eingesetzt. Die Träger-netze wurden mit einem Deckel fixiert, um ein Verrutschen oder Herausfallen aus dem Halter zu verhindern. Anschließend wurde diese Halterung mitsamt den Netzen in der Vakuumverdampfungsanlage über einem Wolframschiffchen mit dem Verdampfungsma-terial so ausgerichtet, dass sich ein Teil der Netze direkt über dem zu verdampfenden Material befand (Reihe A) und die übrigen Netze in größerem Abstand (Reihe B) zu dem Verdampfungsmaterial (siehe Abb. 2.1). Die Vakuumkammer wurde verschlossen und der Druck auf $3 \cdot 10^{-5}$ mbar gebracht. Um die Leistung der Pumpe zu erhöhen, wurde sie während des gesamten Vorgangs mit flüssigem Stickstoff gekühlt. Bei den ersten beiden Bedampfungsprozessen, in denen Silber aufgedampft wurde, wurde dies im Hochvakuum durchgeführt. Alle weiteren Bedampfungsprozesse wurden in Edelgasatmosphäre durchgeführt. Hierfür wurde bei einem Druck von $3 \cdot 10^{-5}$ mbar das Edelgas Argon in die Vakuumkammer geleitet und hierdurch der Druck bis auf $6 \cdot 10^{-3}$ mbar erhöht. Durch Stromzufuhr wurde das Wolframschiffchen, in dem sich das Verdampfungsmaterial befand, bis zur Gelbweißglut erhitzt, was einer Temperatur

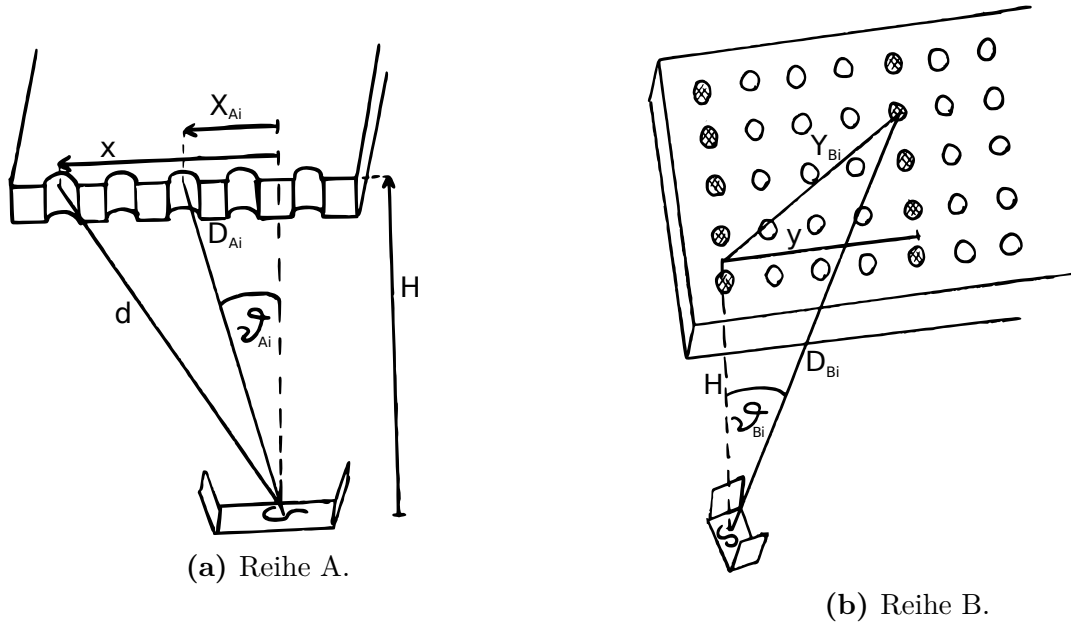


Abbildung 2.2: Ermittlung der Bedampfungswinkel ϑ_{Ai} und ϑ_{Bi} sowie der Bedampfungsabstände D_{Ai} und D_{Bi} .

Verdampfungsmaterial und Trägernetzen zu ermitteln wurde der Abstand zwischen dem zu verdampfenden Material und den Trägernetzen variiert. Der Abstand war durch den Aufbau der Vakuumkammer auf ein Maximum von ca. 15 cm beschränkt. Um die Vergleichbarkeit der Proben zu erhöhen wurden mehrere Trägernetze in einem Herstellungsprozess bedampft. Dadurch herrschten identische Bedingungen bezüglich Druck und Verdampfungsmenge.

2.4 Ermittlung des Verdampfungsabstandes und des Bedampfungswinkels

Vor den einzelnen Verdampfungsprozessen wurde jeweils der Abstand d zwischen dem Netz auf der linken Position in Reihe A und dem Verdampfungsmaterial gemessen. Der Netzhalter wurde so ausgerichtet, dass das Verdampfungsmaterial unter dem vierten und fünften Netz von links gesehen in Reihe A war. Somit konnte im Nachhinein der waagerechte Abstand X_{Ai} zwischen dem jeweiligen Netz dieser Reihe und dem Verdampfungsmaterial ermittelt werden. Aus der Höhe ($H = \sqrt{d^2 - x^2}$) des Halters

mit dem Wert $x = (28,0 \pm 0,1)$ mm für den waagerechten Abstand zwischen dem äußersten linken Netz in dieser Reihe und dem Bedampfungsmaterial wurde der Bedampfungsabstand D_{A_i} zu dem jeweiligen Netz in dieser Reihe wie folgt ermittelt:

$$\begin{aligned} D_{A_i} &= \sqrt{X_{A_i}^2 + H^2} \\ &= \sqrt{X_{A_i}^2 + d^2 - x^2} \end{aligned}$$

Für den Bedampfungswinkel ϑ_{A_i} zwischen den jeweiligen Netzen der Reihe A und dem Verdampfungsmaterial gilt folgende Beziehung:

$$\vartheta_{A_i} = \arcsin\left(\frac{X_{A_i}}{\sqrt{X_{A_i}^2 + d^2 - x^2}}\right).$$

Die Bedampfungsabstände D_{B_i} der Netze in Reihe B wurden wie folgt ermittelt:

$$\begin{aligned} D_{B_i} &= \sqrt{H^2 + Y_{B_i}^2} \\ &= \sqrt{d^2 - x^2 + y^2 + X_{B_i}^2} \end{aligned}$$

Der Abstand y zwischen den Reihen A und B betrug jeweils vom Mittelpunkt der Reihe $(32,0 \pm 0,1)$ mm. Mit der Bedingung $Y_{B_i} = \sqrt{y^2 + X_{B_i}^2}$ für den waagerechten Abstand zwischen dem Verdampfungsmaterial und den jeweiligen Netzen in Reihe B ergibt sich

$$\vartheta_{B_i} = \arctan\left(\frac{\sqrt{y^2 + X_{B_i}^2}}{H}\right)$$

für den Bedampfungswinkel ϑ_{B_i} .

Im Folgenden wird der Bedampfungswinkel zur Vereinfachung als ϑ bezeichnet, da eine Unterscheidung der Reihe beim Bedampfungsprozess im Weiteren nicht notwendig ist. An den Stellen der Auswertung, bei denen die Reihe entscheidend ist, wird explizit darauf hingewiesen.

3 Auswertung

Bei der Herstellung der Proben war der Anteil an unbrauchbaren Proben sehr gering. Lediglich zwei Silber-Proben waren nicht brauchbar, da sie beim Schließen des Halters verrutscht waren. Sie befanden sich somit nicht auf der Öffnung des Halters, wodurch sich beim Verdampfen kein Material auf ihnen ablagern konnte.

Zur Auswertung wurden von jeder einzelnen Probe mehrere Aufnahmen mit dem Transmissionselektronenmikroskop (TEM) Zeiss EM902 gemacht und anschließend mit einer Kamera festgehalten. Bei dem TEM wurde ein Elektronenstrahl erzeugt, der so auf dem Trägernetz mit der Probe eingestellt wurde, dass sich auf dem Schirm ein deutliches Bild der Nanocluster zeigte. Durch Materie im Strahlengang wurde ein Teil des Strahls gestreut und durch die Blenden abgefangen. Da an diesen Stellen weniger Strahlung auf den Schirm traf, erschien die Aufnahme anschließend an dieser Stelle dunkler als an Stellen in der Probe, an denen weniger Material vorhanden war. Da Silber und auch Gold den Strahl stärker beugten als die Trägerschicht (Kohlenstoff), erschienen die Silber- und Gold-Ablagerungen dunkler als die Kohlenstoffträgerschicht auf den Abbildungen.

Bei der Betrachtung der Netze fiel auf, dass sich die Nanocluster auf den einzelnen Netzen jeweils von der Mitte zum Rand hin verkleinerten. Zur besseren Vergleichbarkeit wurden deshalb jeweils die Nanocluster auf dem Mittelpunkt der Netze verglichen und ausgewertet. Da im Nachhinein nicht genau bestimmt werden konnte, in welcher Ausrichtung im Halter sich die Probenträger jeweils bei der Bedampfung befanden, wurde die Veränderung zum Rand hin nicht näher betrachtet. Je nach Ausrichtung der Probenträger war die Abschattung des Netzes größer oder kleiner. Die Zeichnung Abb. 3.1 macht deutlich, welcher Winkel für die Clusterbildung und deren Größen entscheidend war. Beim Aufdampfen war der Winkel ϑ eine entscheidende Größe für die Auswertbarkeit der Proben. Aus der Dicke $(3,0 \pm 0,1)$ mm des Halters und dem Lochdurchmesser $(2,5 \pm 0,1)$ mm ergab sich für den Winkel $\vartheta_{\max} = (22,6 \pm 1,1)^\circ$. Wurde

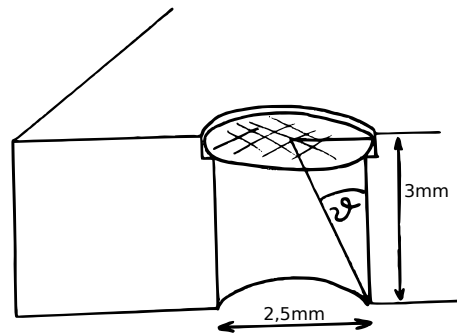


Abbildung 3.1: Probenträger in der Halterung während des Verdampfungsprozesses.

dieser Winkel überschritten, wurden die Probenträger durch den Halter abgeschirmt und die gebildeten Nanocluster waren deutlich kleiner und auch gleichmäßiger in der Größenverteilung als die Nanocluster ohne Abschirmung.

Bei der Betrachtung der Aufnahmen stellten die dunklen Strukturen die Silber- und Goldpartikel dar. Der hellere Hintergrund war die Kohlenstoffschicht, die als Träger der Nanocluster diente. Aufgefallen sind bei der Auswertung der Aufnahmen (neben der Reduktion der Größe zum Rand hin) kleine Partikel zwischen den Nanoclustern. Hierbei handelt es sich um Kristallisationskeime, bei denen es nicht zur Clusterbildung kam [3]. Sie haben sich ebenfalls auf dem Kohlenstoff abgesetzt. Da bei der Auswertung der Größen die Kristallisationskeime nicht einbezogen werden sollten, wurden nur alle Nanocluster ab einer Größe von 10 nm^2 betrachtet.

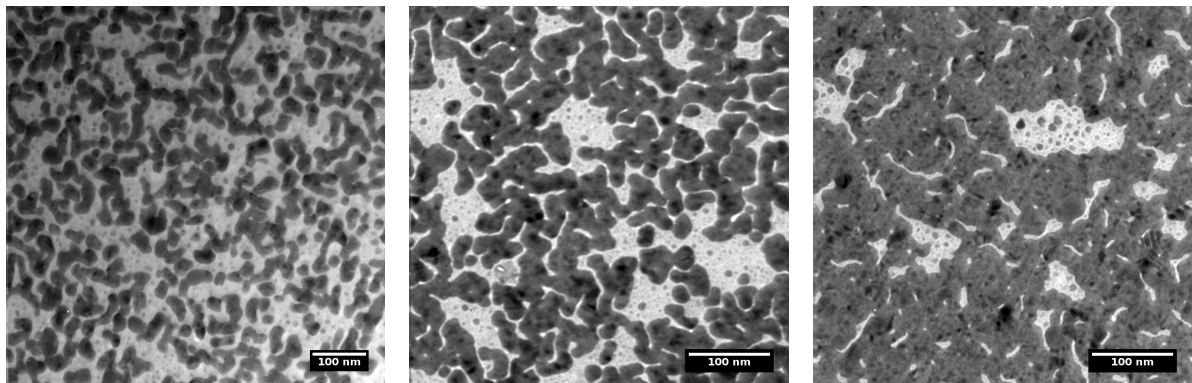
Die Aufnahmen der verschiedenen Proben wurden mit dem Programm Fiji [6] bearbeitet und die mittlere Größe der Nanocluster sowie die Standardabweichung bestimmt. Zuerst wurden Fehler, die durch die Kamera entstanden sind, eliminiert und anschließend die Fläche der einzelnen Nanocluster ermittelt. Bei den Fehlern handelte es sich um weiße und schwarze Flecken, auf den Aufnahmen, die mit der Funktion „Remove Outliers“ entfernt wurden. Um die Flächen der einzelnen Nanocluster zu bestimmen, wurde mit der Funktion „Threshold“ [4] jeweils ein Binärbild erstellt, bei dem die Nanocluster schwarz und der Hintergrund weiß dargestellt wurde. Anschließend wurde von diesen schwarzen Nanoclustern die Fläche bestimmt. Mithilfe eines Tabellenkalkulationsprogramms wurden die Mittelwerte und die Standardabweichungen für jeweils eine Probe berechnet. Da sich die Helligkeit einiger Aufnahmen im Verlauf des Bildes änderte und somit die Kontrastfunktion fehlerhafte Daten verursachte, wurde ein Teil

des Bildes ausgeschnitten und von diesem Ausschnitt die Größen der Nanocluster bestimmt. Da auf diesen Ausschnitten immer noch > 200 Nanocluster abgebildet waren, wurde der hierdurch entstehende Fehler vernachlässigt.

3.1 Silber

3.1.1 Im Hochvakuum hergestellte Silbernanocluster

Zu Beginn der Fertigungsprozesse der Proben wurden zwei Verdampfungsprozesse im Hochvakuum durchgeführt. In Abb. 3.2 sind drei dieser Proben zu sehen. Es ist zu erkennen, dass kaum einzelne Nanocluster vorliegen. Der Großteil der Partikel verwächst miteinander. Lediglich in Abb. 3.2a sind wenige einzelne Nanocluster erkennbar. Da diese Proben nicht zufriedenstellend waren und alle weiteren Proben in Edelgasatmosphäre hergestellt wurden, wurden diese Proben nicht weiter betrachtet. Bei der Auswertung bezüglich Bedampfungsabstand und Verdampfungsmasse wurden sie nicht mit einbezogen.



(a) $D = (8,0 \pm 0,7) \text{ cm}$
 $\vartheta = (20,5 \pm 0,8)^\circ$

(b) $D = (7,6 \pm 0,7) \text{ cm}$
 $\vartheta = (9,1 \pm 0,4)^\circ$

(c) $D = (7,5 \pm 0,7) \text{ cm}$
 $\vartheta = (3,1 \pm 0,2)^\circ$

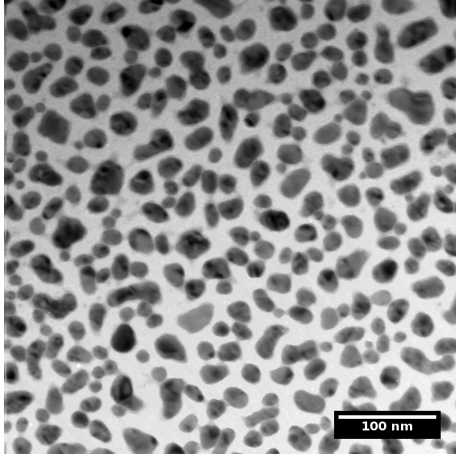
Abbildung 3.2: Im Vakuum gefertigte Ag-Proben;
Verdampfungsmenge $(2,3 \pm 0,1) \text{ mg}$.

3.1.2 In Edelgasatmosphäre hergestellte Silbernanocluster

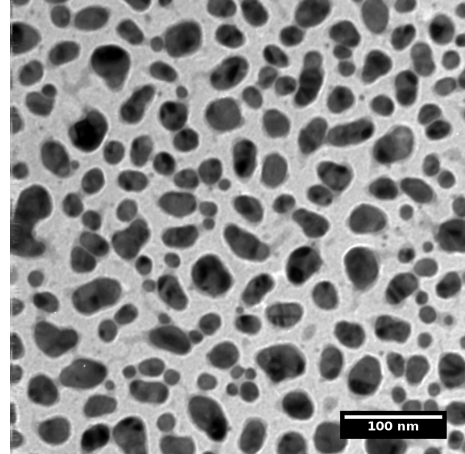
Bei den in Edelgasatmosphäre hergestellten Proben wiesen etliche Proben deutlich Nanocluster auf. Auf einigen Netzen waren die Partikel miteinander verwachsen, zum Teil waren die Netze auch vollständig mit dem Bedampfungsmaterial bedeckt. Die Proben wurden bezüglich der Verdampfungsmenge und des Abstandes zwischen dem Material und den Trägernetzen beim Verdampfungsprozess ausgewertet.

In Abb. 3.3 sind Proben gezeigt, die während eines Aufdampfungsprozesses entstanden sind und in derselben Reihe A des Netzhalters befestigt waren. Somit waren die Verdampfungsmenge und der Edelgasdruck bei dem Aufdampfungsprozess identisch. Die Aufnahmen Abb. 3.3a bis 3.3c sehen recht ähnlich aus; die Verteilung der Nanocluster sowie die durchschnittliche Fläche sind nahezu gleich. Es gibt einzelne Nanocluster und auch einige miteinander verwachsene Cluster. Bei Abb. 3.3a ist im Unterschied zu den anderen drei Aufnahmen zu sehen, dass die Nanocluster einen kleineren Durchmesser haben. Es sind hauptsächlich einzelne Cluster auf dieser Probe zu erkennen. Das Verhältnis zwischen Verdampfungsmenge und Bedampfungsabstand sind hier optimal für die Herstellung von Nanoclustern. Dieser Probenträger war während des Verdampfungsprozesses an der äußersten Stelle der Reihe A des Probenhalters, jedoch haben alle vier Proben den Winkel $\vartheta_{\max}$ überschritten. Durch die Abschirmung des Halters wurden größere Mengen Verdampfungsmaterial abgefangen und konnten nicht zu den Trägern gelangen. Dieses Verhalten konnte im Laufe der Auswertung der verschiedenen Proben häufiger beobachtet werden. Allgemein ist zu sagen, dass unter dem Verhältnis Masse $(0,63 \pm 0,10)$ mg zu Abstand 5,3 cm bis 6 cm gleichmäßige einzelne Nanocluster entstehen. Die Ähnlichkeit der Proben weist auf eine gute Reproduzierbarkeit der Nanocluster hin, was zusätzlich durch weitere Aufdampfungsprozesse mit ähnlichem Ergebnis bestätigt wurde.

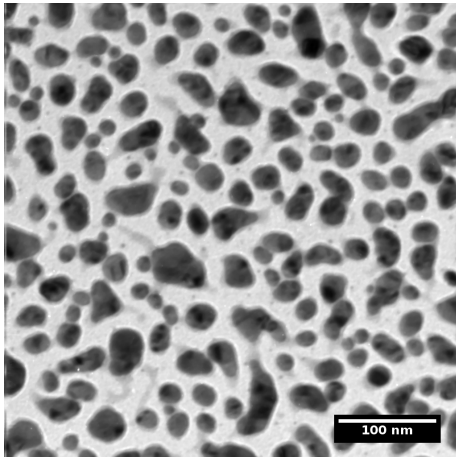
In einer weiteren Herstellungsreihe (Abb. 3.4) wird gezeigt, dass ab einem Abstand von $(5,4 \pm 0,8)$ cm und einer Verdampfungsmenge von $(1,7 \pm 0,1)$ mg keine einzelnen Nanocluster gebildet werden. Die Masse wächst zu einem mäanderförmigen Gebilde zusammen (Abb. 3.4c). Durch den geringen Abstand und die äußere Platzierung in der Reihe beim Aufdampfen wird $\vartheta_{\max}$ überschritten. Bei Abb. 3.4a und 3.4b kommt es, wie schon im vorherigen Beispiel ausgeführt, zu einer Abschattung des Trägernetzes und somit zu Ablagerung kleinerer Partikel.



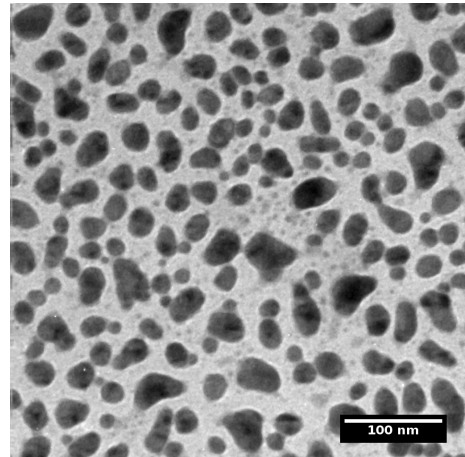
(a) $D = (6,4 \pm 0,7) \text{ cm}$
 $\vartheta = (34,2 \pm 1,7)^\circ$



(b) $D = (6,4 \pm 0,7) \text{ cm}$
 $\vartheta = (33,4 \pm 1,7)^\circ$

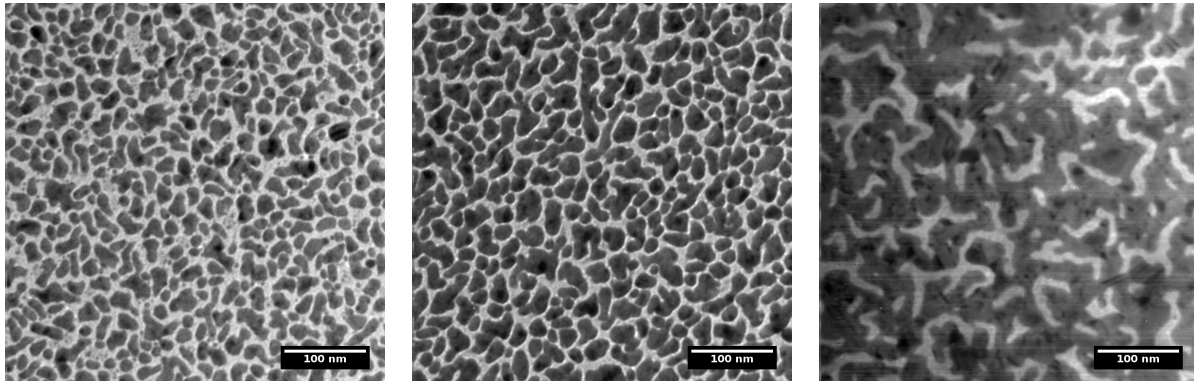


(c) $D = (6,3 \pm 0,7) \text{ cm}$
 $\vartheta = (32,5 \pm 1,7)^\circ$



(d) $D = (6,2 \pm 0,7) \text{ cm}$
 $\vartheta = (31,6 \pm 1,6)^\circ$

Abbildung 3.3: Diese vier Silber-Proben wurden bei einem Herstellungsprozess hergestellt; Verdampfungsmenge $(0,6 \pm 0,1) \text{ mg}$.



(a) $D = (6,0 \pm 0,7) \text{ cm}$
 $\vartheta = (27,8 \pm 1,5)^\circ$

(b) $D = (5,7 \pm 0,7) \text{ cm}$
 $\vartheta = (20,7 \pm 1,2)^\circ$

(c) $D = (5,4 \pm 0,8) \text{ cm}$
 $\vartheta = (12,7 \pm 0,8)^\circ$

Abbildung 3.4: Proben wurden in einem Herstellungsprozess hergestellt. Es wird deutlich, ab welchem Winkel die Cluster zusammenwachsen. Verdampfungsmenge: $(1,7 \pm 0,1) \text{ mg}$ Silber.

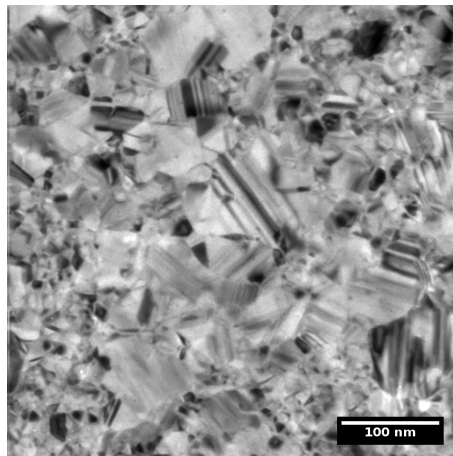


Abbildung 3.5: Komplette bedeckte Silber-Probe;
 Verdampfungsmenge $(2,9 \pm 0,1) \text{ mg}$, $D = 7 \text{ cm}$ bis $6,3 \text{ cm}$.

In Abb. 3.5 ist eine Silberprobe zu sehen, die aufgrund der Materialmenge und des Abstandes während des Herstellungsprozesses komplett bedeckt ist. Es sind einzelne Kristallstrukturen zu erkennen, die während des Herstellungsprozesses zusammengewachsen sind. Aufgrund der kristallinen Struktur kam es zu Braggreflexion, was an den parallelen Linien zu erkennen ist. Die einzelnen Kristalle sind in unterschiedliche Richtungen ausgerichtet. Dieses war nicht Ziel der Arbeit; es ist jedoch interessant zu sehen, dass sich auch bei größeren Mengen an Verdampfungsmaterial Kristallstrukturen ausgebildet haben.

Ein wesentlicher Punkt bei der Auswertung war die Bildung von Nanoclustern. In Abb. 3.6 ist die Bildung von Nanoclustern in Abhängigkeit von der Verdampfungs- und Aufdampfungsabstand aufgeführt. Hierbei ist eine deutliche Abgrenzung zwischen Nanoclustern und verschmolzener Masse zu sehen. Zudem ist zu erkennen, welche Proben in demselben Prozess hergestellt wurden. Sie liegen horizontal auf einer Linie, da die Verdampfungs- und Aufdampfungsabstände identisch waren; lediglich der Aufdampfungsabstand variierte. In Abb. 3.7 sind die Mittelwerte der Größen der Nanocluster aller einzelner Silber-Proben dargestellt. Die Punktgrößen stellen hierbei die durchschnittliche Nanoclustergröße dar. Hierbei wurde unterschieden, in welcher Reihe die Proben aufgedampft wurden. Zu erkennen ist die starke Abnahme der Größe der Nanocluster zwischen benachbarten Proben lediglich durch die Änderung der Reihe beim Aufdampfen. Die Ergebnisse der Silbernanocluster sind nochmals zusammengefasst in Tabelle 3.1. Zur Ermittlung der in Tabelle 3.1 angegebenen Durchmesser wurde eine kreisförmige Fläche zugrunde gelegt. Da die Nanocluster zum Teil sehr stark in ihrer Größe schwankten, ist im Mittelwert jedoch recht klein, ist bei manchen Werten die angegebene Schwankung größer als der eigentliche Wert.

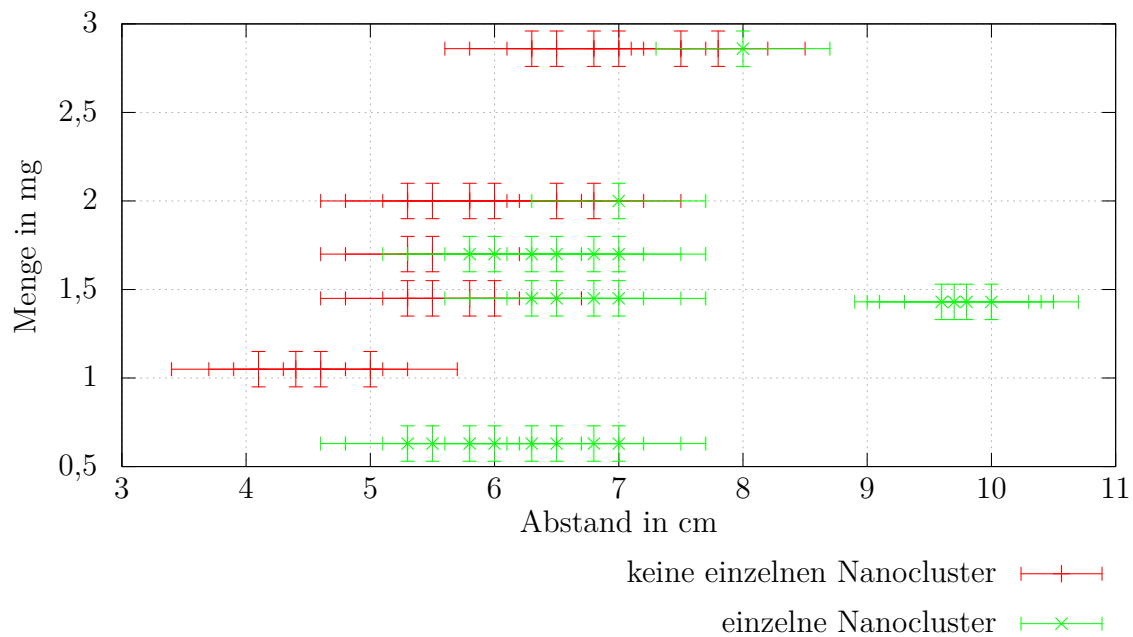


Abbildung 3.6: Verdampfungsmaterial Silber: Nanocluster-Bildung in Abhängigkeit von Materialmenge und Abstand zwischen Material und Trägernetzen.

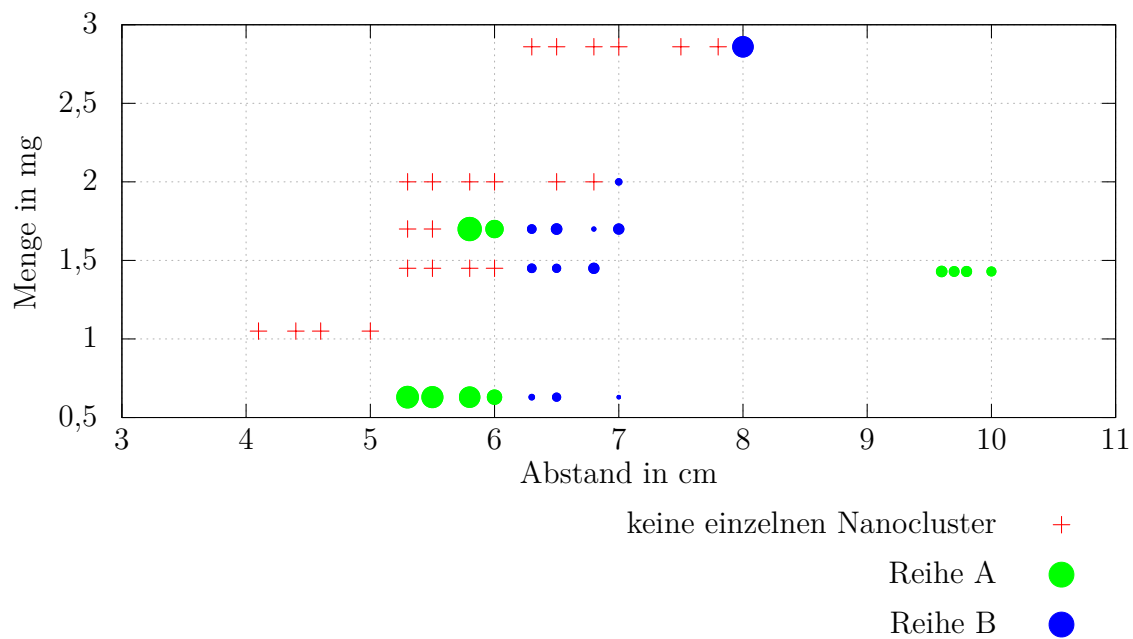
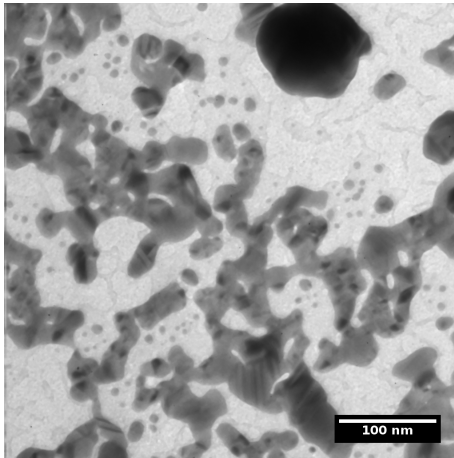


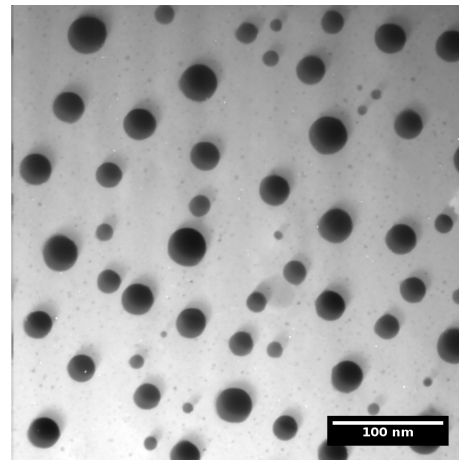
Abbildung 3.7: Verdampfungsmaterial Silber: Größenunterschied der Nanocluster in Abhängigkeit der Reihe des Netzes beim Verdampfungsprozess. Die Punktgrößen stellen in dieser Grafik die durchschnittliche Nanoclustergröße dar.

Tabelle 3.1: Fläche und Durchmesser der Silbernanocluster in Verbindung mit Verdampfungs-
menge und -abstand.

Mittelwert Fläche [nm ²]	Durchmesser [nm]	Abstand [cm]	Menge [mg]	Reihe
140,6 ± 179,1	13,4 ± 8,5	(10–9,6) ± 0,7	1,4 ± 0,1	A
783,0 ± 687,6	31,6 ± 13,9	5,8 ± 0,7	1,7 ± 0,1	A
640,9 ± 410,9	28,6 ± 9,2	(5,8–5,3) ± 0,7	0,6 ± 0,1	A
119,0 ± 57,5	12,3 ± 3,0	(7–6,3) ± 0,7	1,5 ± 0,1	B
140,4 ± 84,0	13,4 ± 4,0	(7–6,3) ± 0,7	1,7 ± 0,1	B
54,0 ± 62,1	8,3 ± 4,8	(7–6,3) ± 0,7	0,6 ± 0,1	B
58,6 ± 36,4	8,6 ± 2,7	7,0 ± 0,7	2,0 ± 0,1	B
608,6 ± 993,3	31,6 ± 13,9	8,0 ± 0,7	2,9 ± 0,1	B



(a) Eine große Silberkugel umgeben von verschmolzenen Silbernanoclustern.

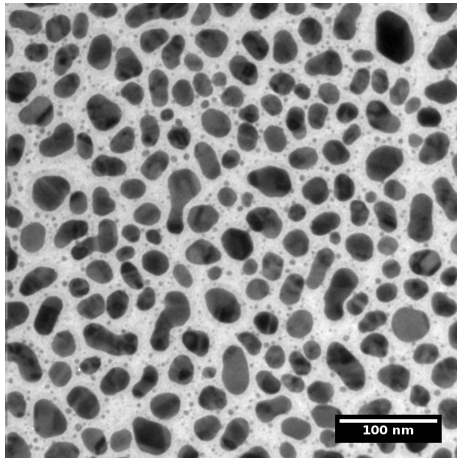


(b) Einzelne Silberkugeln.

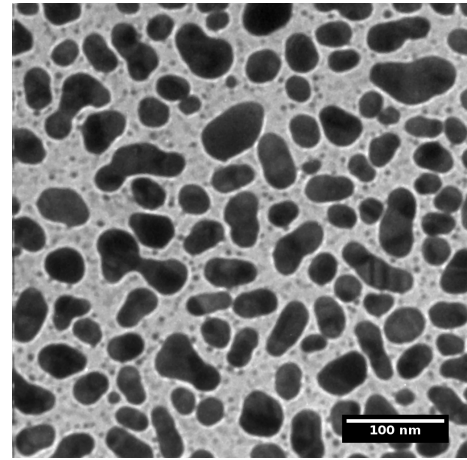
Abbildung 3.8: Kugelbildung auf einer Probe.

3.1.3 Kugelförmige Strukturbildung

Bei einer Probe war auf einem Bereich des Netzes die Struktur der Silbernanopartikel auffällig. Es waren kugelförmige Ablagerungen (Abb. 3.8) zu sehen. Diese kugelförmigen Strukturen waren auf einen Teilbereich der Probe beschränkt und hatten einen fließenden Übergang von Nanoclustern mit vereinzelt Kugeln (Abb. 3.8a) bis hin zu einer reinen Ansammlung von Kugeln (Abb. 3.8b). Möglicherweise wurde auf den Träger gefasst, als er vor dem Bedampfen in den Halter eingesetzt wurde, wodurch eine Fettschicht aufgetragen wurde. Die Silberkugeln erinnern an Wassertropfen auf einer Fettschicht.



(a) $D = (6,0 \pm 0,7) \text{ cm}$
 $\vartheta = (27,8 \pm 1,5)^\circ$



(b) $D = (5,4 \pm 0,8) \text{ cm}$
 $\vartheta = (12,7 \pm 0,8)^\circ$

Abbildung 3.9: Goldnanocluster eines Herstellungsprozesses;
Verdampfungsmenge $(1,4 \pm 0,1) \text{ mg}$.

3.2 Gold

Alle Goldproben wurden in Edelgasatmosphäre aufgedampft, da bereits bei den Silberproben die Nanoclusterbildung in Edelgasatmosphäre bessere Ergebnisse ergab als die Herstellung im Hochvakuum. Es hat sich bei den ersten hergestellten Proben schon eine gute Bildung von Nanoclustern gezeigt, so dass dieses Verfahren beibehalten wurde. Beim Verdampfungsprozess waren die Probenträger ebenfalls in den Reihen A und B angeordnet.

In Abb. 3.9 sind zwei Proben zu sehen, bei denen sich einzelne Nanocluster gebildet haben, wenige sind zusammengeschlossen. Diese Proben wurden in einem Abstand von 5,3 cm bis 6 cm und der Verdampfung von $(1,36 \pm 0,10) \text{ mg}$ aufgedampft. Auch die Ablagerungen der Kristallisationskeime sind zwischen den Nanoclustern erkennbar.

Unterschiedliche Phasen der Nanocluster werden in Abb. 3.10 gezeigt; einzelne Nanocluster sind in Abb. 3.10c und 3.10d zu sehen und der Beginn des Zusammenwachsens von Nanoclustern ist in Abb. 3.10b dargestellt. In Abb. 3.10a sind die Nanocluster nicht mehr einzeln vorhanden, sondern bilden eine mäanderförmige Struktur. Bei diesen Proben war, wie schon bei den Silberproben, die Abschattung durch die Halterung beim Aufdampfungsprozess ein entscheidender Faktor zwischen Nanoclusterbildung

Introduction

1.1 Transmission Electron Microscopy

1.1.1 Conventional Transmission Electron Microscopy

In a conventional transmission electron microscope (CTEM, or TEM for short) (Fig. 1.1), a thin specimen is irradiated with an electron beam of uniform current density. The acceleration voltage of routine instruments is 100–200 kV. Medium-voltage instruments work at 200–500 kV to provide better transmission and resolution, and in high-voltage electron microscopy (HVEM) the acceleration voltage reaches 500 kV–3 MV. Earlier books on the subject are listed as references [1.1–1.55]. The development of both theory and instrumentation as well as the different applications of TEM can be followed by consulting the proceedings of the International Conferences on Electron Microscopy [1.56–1.68].

Electrons are emitted in the electron gun by thermionic, Schottky, or field emission. The latter are used when high gun brightness and coherence are needed. A three- or four-stage condenser-lens system permits variation of the illumination aperture and the area of the specimen illuminated. The electron-intensity distribution behind the specimen is imaged with a lens system, composed of three to eight lenses, onto a fluorescent screen. The image can be recorded by direct exposure of a photographic emulsion or an image plate inside the vacuum, or digitally via a fluorescent screen coupled by a fiber-optic plate to a CCD camera.

Electrons interact strongly with atoms by elastic and inelastic scattering. The specimen must therefore be very thin, typically of the order of 5–100 nm for 100 keV electrons, depending on the density and elemental composition of the object and the resolution desired. Special preparation techniques are needed for this; electropolishing and ion-beam etching in materials science and ultramicrotomy of stained and embedded tissues or cryofixation in the biosciences.

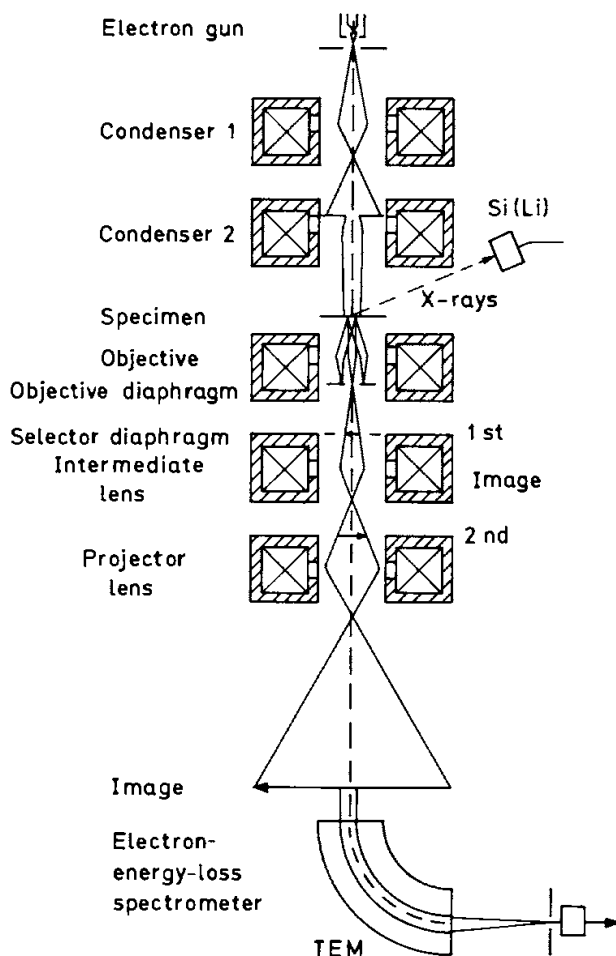


Fig. 1.1. Schematic ray path for a transmission electron microscope (TEM) equipped for additional x-ray and electron energy-loss spectroscopy.

The aberrations of the objective lens are so great that it is necessary to work with very small objective apertures, of the order of 10–25 mrad, to achieve a resolution of the order of 0.1–0.3 nm. Bright-field contrast is produced either by intercepting the electrons scattered through angles larger than the objective aperture (scattering contrast) or by interference between the scattered wave and the incident wave at the image point (phase contrast). The phase of the electron waves behind the specimen is modified by the wave aberration of the objective lens. This aberration and the energy spread of the electron gun, which is of the order of 0.3–2 eV, limit the contrast transfer of high spatial frequencies. Dark-field contrast is obtained by tilting the primary beam or by hollow-cone illumination so that the primary beam falls on the objective diaphragm.

In crystalline specimens, the use of the primary beam (bright field) or a Bragg-reflected beam on-axis (dark field) gives rise to diffraction contrast, which is important for the imaging of crystal defects. When Bragg-diffracted beams also pass through the aperture, crystal-structure imaging reveals projections of atomic rows. For the interpretation of these images, digital image simulation using the dynamical theory of electron diffraction is indispensable.

A further capability of modern TEM is the formation of nanometer-sized electron probes, 0.2–10 nm in diameter, by means of a three- or four-stage condenser-lens system, the last lens field of which is the objective prefield in front of the specimen. The main applications of such electron probes are in analytical electron microscopy (see below). This enables the instrument to operate in the scanning transmission (STEM) mode with a resolution determined by the electron-probe diameter; this has advantages for imaging thick specimens and for recording secondary electrons and backscattered electrons.

1.1.2 High-Resolution Electron Microscopy

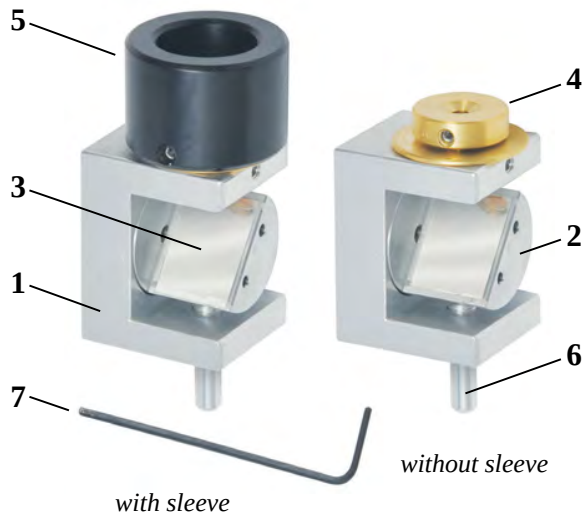
The wave-optical theory of imaging is necessary to discuss high resolution. This theory can be expressed in terms of a two-stage Fourier transform. In the focal plane of the objective lens, the diffraction pattern of the specimen is formed; each scattering angle θ corresponds reciprocally to a periodic spacing Λ in the specimen, or in other words is proportional to a spatial frequency $q = 1/\Lambda$ since $\theta \simeq \lambda/\Lambda = \lambda q$ (λ : electron wavelength). The amplitude distribution $F(q)$ of the electron wave in the focal plane is the Fourier transform of the specimen transparency. The spherical aberration can be represented as a wave aberration, which is an additional phase shift that depends on scattering angle, the spherical-aberration constant C_s , and the defocusing Δz . This phase shift can be introduced as a phase factor applied to $F(q)$. The image amplitude is then the inverse Fourier transform of this weighted Fourier transform, in which the influences of the diaphragm, the finite illumination aperture (partial spatial coherence), and the energy spread of the electron gun (partial temporal coherence) can be included. The result may be expressed in terms of a contrast-transfer function for the different spatial frequencies. This transfer function is important because it characterizes the effect of the instrument on image formation and is independent of the particular specimen in question.

Transmission electron microscopy can provide high resolution [1.69, 1.70] because elastic scattering is an interaction process that is highly localized to the region occupied by the screened Coulomb potential of an atomic nucleus. The angular distribution of inelastically scattered electrons is concentrated within smaller scattering angles than that of elastically scattered electrons. Most of the inelastically scattered electrons normally pass through the objective diaphragm in the bright-field mode. Inelastically scattered electrons do not, however, contribute to high-resolution image details because the inelastic scattering is less localized. With increasing energy loss, the localization becomes narrower for inner-shell ionization, and resolutions of lattice periodicities of about 0.3–0.5 nm are possible with energy-filtering transmission electron microscopy.

The spherical-aberration coefficients C_s in present-day microscopes are about 0.5–2 mm. The optimum imaging condition in bright-field mode occurs at the Scherzer defocus $\Delta z = (C_s \lambda)^{1/2}$, for which a broad band of spatial

PELCO® STEM Imaging Holder - Instructions

Product No. 16412 and 16412-4



Components of the PELCO® STEM Imaging Holder

1. Aluminum frame
2. Adjustable aluminum conversion plate holder
3. Platinum conversion plate
4. TEM grid holder assembly with aperture
5. Anti-scatter sleeve (conductive plastic)
6. Optional pin (3.2 x 9.5mm)
7. Hex key for set screws

Positioning and use of the PELCO® STEM Imaging Holder

Before using the PELCO® STEM Imaging Holder, the user has to determine if it will fit in the SEM chamber and can be moved without damaging any existing parts in the SEM chamber. It might be advisable to retract EDX and BSE detectors.

The PELCO® STEM Imaging Holder has to be aligned with the E-beam axis so that the E-beam can scan the TEM sample. The frame has to be rotated (use stage rotation) in such a way that the conversion plate faces towards the SE detector. The conversion plate angle can be adjusted by loosening the screw on base using a #1 Phillips screwdriver and adjusting to optimize SE detection. For most applications a 45° angle would be sufficient. If the SE detector is positioned lower than the conversion plate, a higher angle might be chosen.

An angle lower than 45° is not advisable; the frame might block part of the SE electrons. (Angle definition: conversion plate vertical is 90°, conversion plate horizontal is 0°).

It is strongly recommended to use the anti-scatter sleeve. This will prevent secondary electrons, generated at the surface (topside) being detected by the SE detector. When used, move the STEM imaging detector up to have the top of the anti-scatter sleeve as close as possible to the pole piece without touching the pole piece if any detector mounted on or close to the pole piece.

Sample Loading (see next page)

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Loading a Sample in the PELCO® STEM Imaging Holder



1. Loosen set screw and remove anti-scatter sleeve.



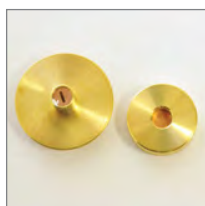
2. Loosen set screw base and remove TEM grid holder with aperture.



3. Place grid holder, top side down on flat surface.
4. Loosen set screw on grid holder top and lift off bottom component of grid holder.



5. Place 3.05mm TEM grid into recess in grid holder top, sample side down (will be incident beam side up when installed in microscope).



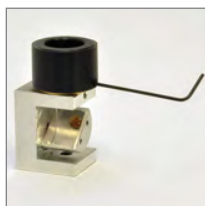
6. TEM grid shown placed into recess in grid holder top.



7. Re-insert grid holder bottom into grid holder top and tighten set screw.



8. Replace grid holder unit into base and tighten set screw.



9. Replace anti-scatter sleeve onto base, over grid holder and tighten set screw.

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