

# Week 3

???

## 3.1 Diamond Anvil Cell + Scanning Electron Microscopy

- 1/17:
- There will be a demonstration class with Dr. Filatov some afternoon. He will show us how to run some experiments, both sample-wise and data-wise.
  - Review of DAC content from last class.
  - Diamond anvil cell program and GSECARRs.
    - UChicago's dedicated beamline is Sector 13.
    - It pulls electrons out of the storage ring using IDs or BMs.
    - “S” on this slide stands for single-crystal.
    - DACs are now automated to a very large extent; no more manual screw adjustment.
  - An example experiment: Phase relations of iron carbides at high temperatures and pressures.
    - You don't need to remember this; it's just to give you a flavor of what can be done.
    - These compounds are applicable to geology since they're often far in the ground.
    - DACs and laser heating replicate the heat and pressure present deep in the earth.
    - The researchers built a phase diagram from the XRD spectra of both solid and liquid phases.
    - Main takeaway: You can study more than crystalline phase transitions; indeed, even solid-to-liquid transitions are on the table.
  - Another example experiment: Magnesium peroxide formation.
    - Magnesium peroxide is present in some geological objects.
    - In these experiments, researchers recreated the conditions that can cause the geological formation of  $\text{MgO}_2$  over  $\text{MgO}$  to observe how it happens.
  - One more example experiment:  $\text{NaCl}$  stoichiometry
    - Published in Science: You'd think it'd be hard to be surprised by a result about  $\text{NaCl}$  at this point, but these scientists proved the existence of  $\text{Na}_3\text{Cl}$  and  $\text{NaCl}_3$  at high pressures.
    - $\text{Na}_3\text{Cl}$  is composed of layers of pure sodium and layers of  $\text{NaCl}$ .
    - These new “isomers” have special properties, e.g., the pure sodium layer in  $\text{Na}_3\text{Cl}$  conducts electricity in two-dimensions, and the surrounding  $\text{NaCl}$  layers act as insulators.
    - Good follow-up question: What is the charge? Could  $\text{Na}_3\text{Cl}$ , for instance, still be neutral?
    - Shevchenko recommends we check out the paper: Zhang et al. (2013).

- Challenges for DAC studies.
  - Chemical reaction of sample/medium with diamond.
    - Especially prevalent with alkali metals and hydrogen.
  - Any imperfections in the diamond anvil culet surface cause them to easily crack.
    - Cracking the diamond forces you not just to get new diamonds (expensive), but to have to restart your experiment (costly in terms of time).
  - Hydrogen penetrates the metal gasket and diamond anvils easily at higher temperatures and pressures.
  - Solution: Use cryogenic temperatures (just slow down the process).
    - Even in this case, you can still do heating experiments; you just have to *locally* heat your sample.
- Synthesis of new materials.
  - Procedure: Synthesize a material, create possible models of it, calculate the predicted XRD pattern, test alignment with the actual XRD pattern.
  - Example:  $\text{NaH}_3$  with elongated molecules of  $\text{H}_2$  incorporated into the crystal lattice.
- First DAC experiments on nanomaterials.
  - First conducted by Sarah H. Tolbert (now a UCLA prof) and A. P. Alivisatos in 1995.
  - Examined pressure-induced structural transformations in semiconductor nanocrystals.
  - Observed elevation in solid-solid structural transformation pressure as crystallite size decreases.
  - Example: CdSe nanocrystals.
    - The CdSe nanocrystals undergo a wurtzite to rock salt transition (similar to bulk CdSe).
    - The nanocrystal phase transition pressures varied from 3.6-4.9 GPa for crystallites ranging from 21-10 Å in radius (bulk CdSe: 2.0 GPa).
    - Demonstrated that the transition only nucleates once in each nanocrystal.
- Probing of mechanical properties using DAC.
  - DACs are often used to probe nanoparticle assemblies.
  - NPs can be assembled into periodic structures (recall the first class).
  - Compress a ruby and PbS up to 50 GPa.
  - Can you bring NPs close enough together to observe collective properties? At close enough distances, the organic strings around them intercalate. Can you push them even closer?
  - The computer simulations of this took much longer than the actual DAC experiment.
  - Removing pressure allows elastic recovery.
  - Conclusions: In this case, we could not bring particles close enough together to observe collected properties. Not conclusive though; maybe other ligands, more pressure would work.
- High-pressure structural stability and elasticity.
  - Many cases of using DACs to study structures made out of gold or CoO particles.
  - Recall that NPs are often single crystals.
  - NPs can have a preferred orientation when we compress them.
- Mechanical stability of crystals assembled from  $\text{Fe}_x\text{O}_y$  NPs.
  - Vacant, polycrystalline shells should implode/explode upon isotropic compression, but instead they are very stable (maybe something to do with the spherical shape).

- How “hollow” are hollow  $\text{Fe}_x\text{O}_y$  NPs?
  - Alivisatos is often mentioned in this course because he did actually play a very big role in the development of nanoscience.
  - This example is from Shevchenko’s own work.
  - At high temperatures, NPs start to seed; you end up with large blobs. Thus, reactivity goes down (if you’ve got catalysts mounted on their surface).
  - The shell is not penetrable to gases.
    - Pores (defects) can allow gases to enter in theory, though.
  - Inside the shell, there are tiny fragment of Fe or  $\text{Fe}_x\text{O}_y$ .
  - These particles are hoped to be able to deliver drugs since they have pores.
  - If He or Ne diffuses into the NPs, we know that Ne crystallizes upon compression, so if it goes into the NPs, then you start to see broader peaks (relation to Figure 2.14??).
  - This was not observed, so Shevchenko concluded that  $\text{Fe}_x\text{O}_y$  shells do not allow the transport of atoms in and out.
- Pressure-mediated doping in graphene.
  - Alcohol was used as a pressure transmitting media.
  - Raman spectroscopy monitored the transition in graphene.
  - Conclusion: Alcohol can dope graphene upon compression.
  - No doping is observed when Ar is used as a pressure transmitting medium.
  - First reported in 2011 (when graphene was exploding); mechanism in 2017.
  - Conclusion: Electron charge injection is through the  $\text{SiO}_2$  substrate.
  - The formation of silanol groups ( $\text{Si}-\text{O}-\text{H}$ ) on the surface of oxidized silicon substrates (similar to CNTs) — origin of doping in graphene.
- Pressure studies on MOFs.
  - Since MOFs are promising for separation (which requires compression at some point), researchers wanted to know how they behave under compression.
  - Different behavior under pressure? And can liquid get inside MOF shells under pressure?
  - Pressure-transmitting medium 1 was NaCl: Irreversible amorphization (collapsing) of the empty structure occurs at about 0.4 GPa.
  - Pressure-transmitting medium 2 was oil: Slight lattice expansion and a strong modification of the peak frequency and shape of the MOF hydroxyl vibration below 0.1 GPa.
  - Pressure-transmitting medium 3 was high-viscosity polydimethylsiloxane silicone oil: Framework stability is enhanced under pressure with the amorphization onset shifted to about 7 GPa.
- Why were the media from previous selected?

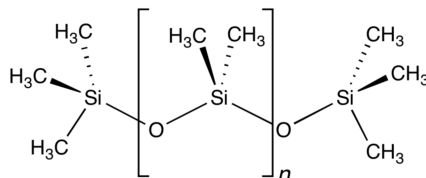


Figure 3.1: Polydimethylsiloxane silicone oil.

- NaCl: Optically transparent in the study areas, so minimal background interference.
- Nujol: An inert mineral oil used in infrared spectroscopy. It has a relatively simple IR spectrum.
- Polydimethylsiloxane silicone oil: Inert and optically transparent.
- You have to be sure that your medium does not overlap with your sample.
- Pressure-mediated changes in MOFs.

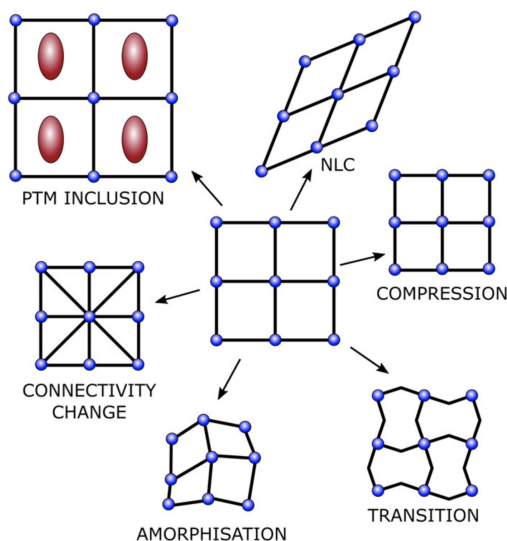


Figure 3.2: MOFs under extreme pressure.

- Negative linear compressibility (NLC).
  - Either causes expansion or net zero compressibility (compressibility along one or two axes, expansion along two or one).
- Compression.
- Transition.
- Amorphisation.
  - Note that transition preserves crystallinity in some form, while amorphisation does away with it entirely.
- Connectivity change.
- Pressure-transmitting medium (PTM) inclusion.
- Summary of DAC studies.
  - Use them to...
    - Study phase transformation;
    - Study the synthesis of novel materials;
    - Understand the universe/the formation of extant Earthbound or extraterrestrial minerals.
- We now move on to scanning electron microscopy.
- Examples of SEM images.
  - Pollen from different plants, the eye of a fruit fly, and opal.
    - Note that opal is made of (possible fused) silicon beads of either uniform or different sizes.
  - False color: Allows you to highlight certain features.

- First SEM.
  - The concepts was first proposed in 1935 by Max Knoll.
  - At the time, researchers were actively working on using electrons for imaging but were focusing on transmission.
  - Manfred von Ardenne designed the first scanning transmission electron microscope (STEM) in 1937-38 by adding scan coils to a transmission electron microscope to surpass its resolution.
  - The first STEM micrograph depicts ZnO crystals imaged at an operating voltage of 23 kV at a magnification of 8000 times, and a spatial resolution between 50-100 nm.
    - Nowadays, the resolution is about 1.5 nm.
  - Keep in mind that SEM and STEM are different.
- Interactions of electrons with matter.

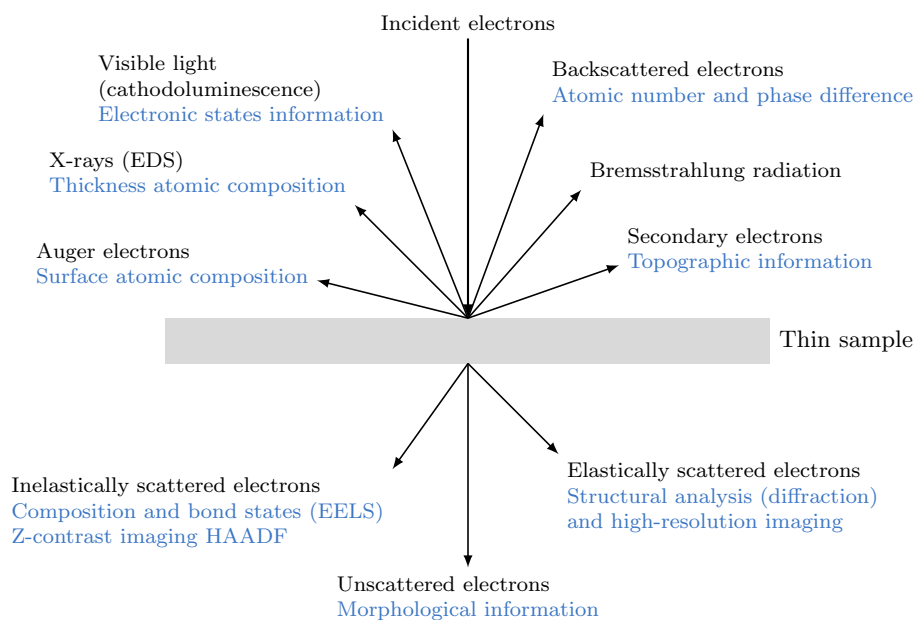


Figure 3.3: Interaction of electrons with matter.

- Consider a thin sample.
- We can cause a whole bunch of changes in our material with incoming electrons.
- We will talk about all of these eventually.
- SEM uses **backscattered electrons** and **secondary electrons**.
- **Secondary electron**: An electron knocked out of a substance by a separate incident electron. *Also known as SE.*
- **Backscattered electron**: An incident electron that gets rerouted back in the original direction via a close encounter with the nucleus. *Also known as BSE.*
  - Thing “gravitational assist” from rocketry.
- Bohr atomic model.
  - Very simplistic, but says what we need. Shevchenko reviews Figure 1.8.
  - Generation of characteristic X-rays, depth profiles, and other phenomena.

- Electron interaction volume within a sample.

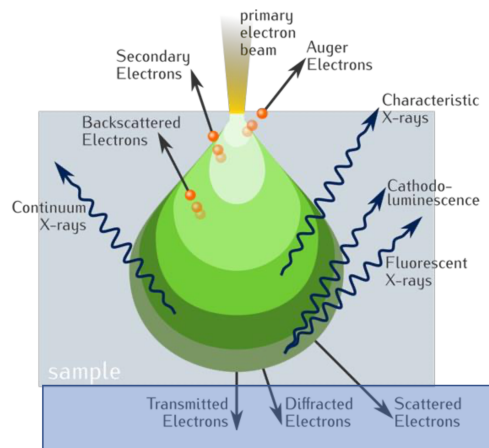


Figure 3.4: Electron interaction volume within a sample.

- **Auger electrons** are only generated at the very very top of the sample.
- The beam electron may be scattered inelastically by the Coulomb field of an atomic nucleus, losing some of its energy in the process as Bremsstrahlung radiation.
- The beam electrons can give up any amount of energy, so the energy distribution of the emitted X-ray is continuous up to the beam energy.
- **Auger electron:** An electron that escapes its atom via the following process. *Also known as AE.*
  1. Incident electrons heat the atom.
  2. A core electron gets removed.
  3. A higher energy electron falls down, releasing energy as it does so.
  4. This energy is not released in the form of light, but is transferred to the electron of interest and used to escape.
- Example: Nickel.
  - Conditions.
    - Sample is predominantly  $Z = 28$ .
    - Accelerating voltage is 20 kV.
    - $0^\circ$  tilt, i.e., incident beam is normal to specimen surface.
  - Penetrations.
    - Augers: Only 10-30 Å.
    - Secondaries: Up to 100 Å.
    - Backscattered:  $< 1 - 2 \mu\text{m}$ .
    - Range of electron penetration: About  $5 \mu\text{m}$  in total.
- Secondary electrons.
  - Often perform the SEM imaging.
  - The electrons, once ionized, often leave the atom with a very small kinetic energy ( $\sim 5 \text{ eV}$ ).
  - There is only a slight energy loss and trajectory change in the incident electron; thus, each incident electron can produce several secondary electrons.
  - Collection of these electrons is aided by using a **collector** in conjunction with the SE detector.

- **Collector:** A grid or mesh with a 100 V potential applied to it which is placed in front of the detector, attracting the negatively charged secondary electrons to it which then pass through the grid holes and into the detector to be counted.
- Secondary electrons for imaging.
  - Mostly effective up to 5 nm in the material.
  - Indeed, secondary electrons provide **surface topology imaging**.
    - Due to their low energy, only SEs that are close to the surface can exit the sample.
    - This small distance enables fine resolution in the SEM.
  - However, secondary electrons provide little-to-no information about elemental contribution.
  - How does a detector tell electrons from the sample vs. the beam?
    - We arrange the detector so that it only picks up electrons from one specific direction, and we control the direction to choose only electrons that are coming up at a particular angle.
  - Lighter elements have greater penetration depths.
  - Secondary electrons are basically ionized electrons.
- Imaging with secondary electrons.
  - Extremely popular with nanofabrication.
- Backscattered electrons (BSE).
  - Elastic scattering happens with little loss of energy.
  - BSEs provide elemental information since the number of BSEs produced is proportional to the atomic number of the elements within the specimen.
    - Higher-atomic number elements “produce” more backscattered electrons and appear brighter than lower atomic number elements.
    - This interaction is utilized to differentiate parts of the specimen that have different average atomic number.
  - Very popular for imaging metal alloys.
- Imaging with backscattered electrons.
  - We don’t know flat vs. texture, but we can still see contrast in the images.
  - In the picture in the slides, we can make out pores, as well as differentiate Mo-rich (lighter colored) regions from Si-rich (darker colored) regions.
    - Since Mo is higher-*Z* than Si, it makes sense that it should be lighter.
- Backscattered electrons vs. secondary electrons.
  - Comparison of images for different alloys.
  - SEs provide more information on the topology of the material.
    - This information *can* coincide with elemental information, but it does not have to.
- Characteristic X-rays.
  - Utilized for elemental analysis since they’re *characteristic*.
  - We have already discussed how these are generated.
  - When electrons are not from the inner shell, an electron drops down, releasing energy in the form of photons in the process.
  - Not relevant to SEM imaging; just elemental analysis.

- Analytical use of characteristic X-rays.
  - EDS=EDX: Energy dispersive spectroscopy and energy dispersive X-ray.
  - Qualitative and quantitative analysis.
  - EDS systems: X-ray detector plus software to collect and analyze energy spectra.
    - Use Si-Li detectors, aka “silicon drift” detectors.
    - Sometimes, such detectors need cooling systems. These are annoying to deal with, and thus are not present in more expensive models that use better, more idealized materials instead.
  - Working principle of the detector: The X-ray absorption converts the energy of individual X-rays into electrical voltages of proportional size.
    - Incoming photons ionize the detector material, yielding free electrons in the crystal.
    - The crystal becomes conductive and produces an electrical charge bias.
    - The electrical pulses correspond to the characteristic X-rays of the element.
- Chemical information (EDS).
  - Spectra, elemental mapping, and line scans.
- Bremsstrahlung.
  - Review of Figures 1.6-1.7.
- Auger electrons (AE).
  - Auger spectroscopy (AES) is liked by some researchers and is rapidly evolving right now.
    - Carries information about the surface of the specimen (the first few atomic layers).
  - Since orbital energies are unique to an atom of a specific element, ejected electrons carry specific chemical information about the surface.
- Building blocks of SEM.
  - Electron source.
  - Limiting apertures surround...
  - Condenser lenses 1-2.
    - These lenses focus them on a spot.
  - Then scanning coils.
  - Lastly, an objective lens focuses everything downward.
  - Three detectors.
    - The BSE detector: A ring surrounding the point at which the incident electrons enter.
    - The SE detector.
    - The EDS detector.
  - These machines are big.
  - The BSE detector is positioned as such so that it can catch backscattered electrons that circle around the nucleus and return close to their original trajectory.
  - The apparatus doesn't move, but the beam does.
  - The detectors stay where they are; you just change the beam position.
  - By varying the current passing through the coils with the time, the position of the beam can be shifted (rastered).
  - Many elements are similar to those in CTEM, but SEM images are not obtained all at once; rather, they are created in a rastering mode.



- SEM resolution.
  - High-Z materials have less penetration.
  - More KE leads to a deeper penetration.
  - Condenser lenses (1-2) focus the beam to a spot of  $\sim 0.4 - 5$  nm, and they determine the focus of the instrument.
  - Resolution can be limited by the interactions of electrons and materials.
    - Dirty samples deposit carbon inside the instrument, spoiling the vacuum and harming the machine.
    - Always be careful! Dirty samples are the product of lazy scientists.
  - Interaction volume depends on material: High-Z materials have smaller interaction volumes.
  - Interaction volume also depends on voltage.
    - More voltage means a higher depth profile (may not be a good thing; for topology, you only want to study only the top surface).
- Astigmatism of your images.
  - Takes place when a lens field is not symmetrical in strength (weaker in one place than in another).
  - Origins of astigmatism.
    - Imperfect polepiece boring.
    - Nonhomogeneous blending of polepiece materials.
    - Dirt on the polepieces, apertures, and/or specimen holders (most common).
  - Solution: A stigmator can be used to selectively correct the field.
    - Stigmators produce weak fields compared to the electromagnetic lenses they correct.
- Detection of astigmatism.
  - Underfocusing the objective lens: Image details line up with the beam shape at that focus.
  - Overfocusing: Image details line up along a direction orthogonal to the underfocused image.
  - At exact focus: Image is OK-ish, but not really as sharp as it could be because the probe size (e.g., condensor) is larger than it should be.
  - Essentially, turn the knob different ways until you get exact focus.
- The last slide on astigmatism.

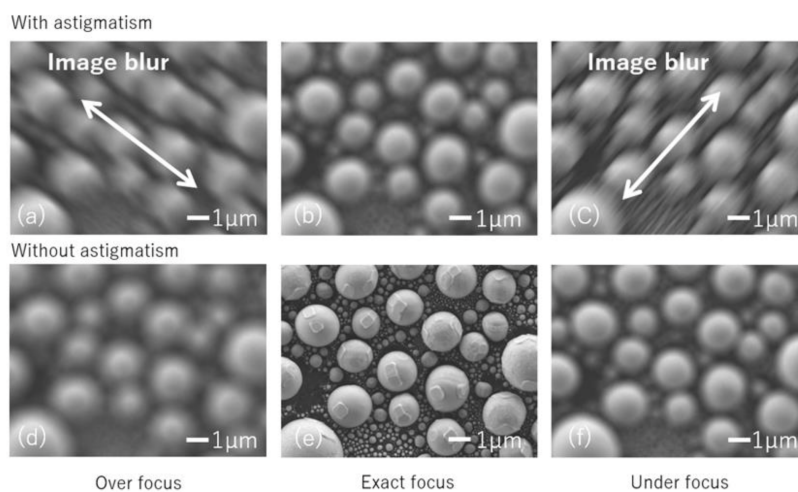


Figure 3.5: Correcting astigmatism.

- It is really important to have good focus.