Crystallography Overview for MEMS
Primary Knowledge (PK)
Participant Guide

Description and Estimated Time to Complete

The *purpose of this learning module* is to introduce the science of crystallography and its importance to microtechnology. Activities provide additional exploration into crystallography and its applications.

This PK unit reviews the science of crystallography as it relates to the construction of microsystem (MEMS) components. You will study three types of solids (amorphous, polycrystalline, and crystalline) and will learn how to identify crystal orientation based on Miller indices.

Estimated Time to Complete
Allow about 40 minutes

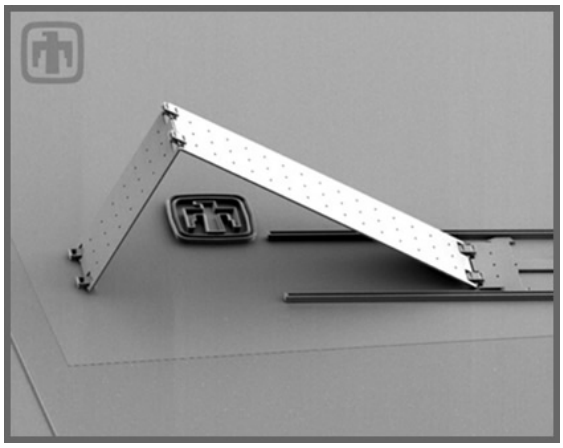
Introduction

Crystallography is the science of determining the arrangement of atoms in solid matter. Solids with an irregular arrangement of atoms are amorphous or noncrystalline structures. Such solids include glass, soot, plastics, and gels. Solids composed of atoms arranged in a definite pattern with a repeating structure are crystalline structures. These structures include diamonds, ice, quartz, and an old favorite, rock candy. All solid matter is either amorphous or crystalline, or a type of crystalline matter called polycrystalline.

One of the objects below is amorphous. The other is crystalline. *Which is which?*

Pretty obvious, isn't it? *Notice the cloudiness of the amorphous glass (bottom left) compared to the clarity of the crystalline diamond (top right).*

Because the atoms of crystalline structures "fit together" so well, a crystal is typically very strong. This characteristic is invaluable for the construction of micro and nanosized devices. The fabrication of microsystems requires a type of crystalline substrate in order to build microsized structures such as cantilevers, diaphragms, gears, comb drives, and electronic circuits. The image to the right is a MEMS popup mirror used to redirect optical data.



MEMS popup mirror
[Courtesy of Sandia National Laboratories, SUMMIT Technologies, www.mems.sandia.gov]

This unit discusses three topics of crystallography:

- The types of solid matter (amorphous, polycrystalline and crystalline)
- Miller Indices (a method of describing planes and directions within a crystal)
- Growing crystals

Objectives

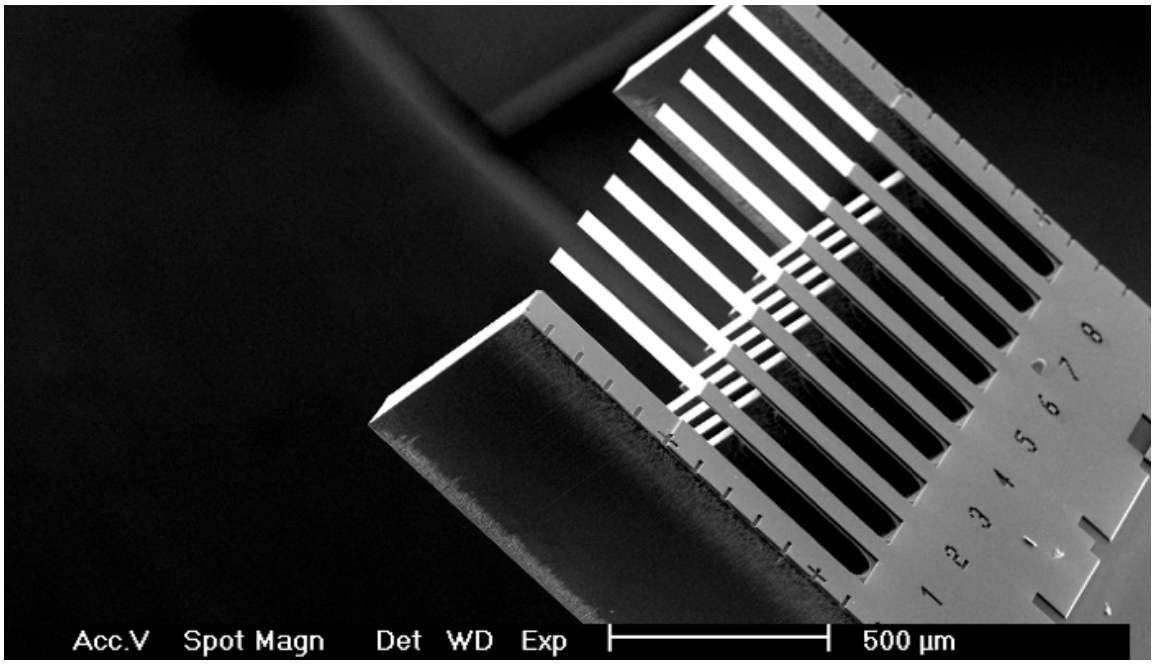
- State at least one example for each type of solid matter (amorphous, polycrystalline and crystalline).
- Discuss the importance of crystal structures in MEMS fabrication.
- Identify the direction of a crystal plane using the Miller index notation.

Key Terms (The key terms are defined in the glossary at this end of this unit.)

Amorphous
Crystalline
Crystallography
Grains
Grain Boundaries
Miller Indices
Polycrystalline
Unit cell

Crystallography

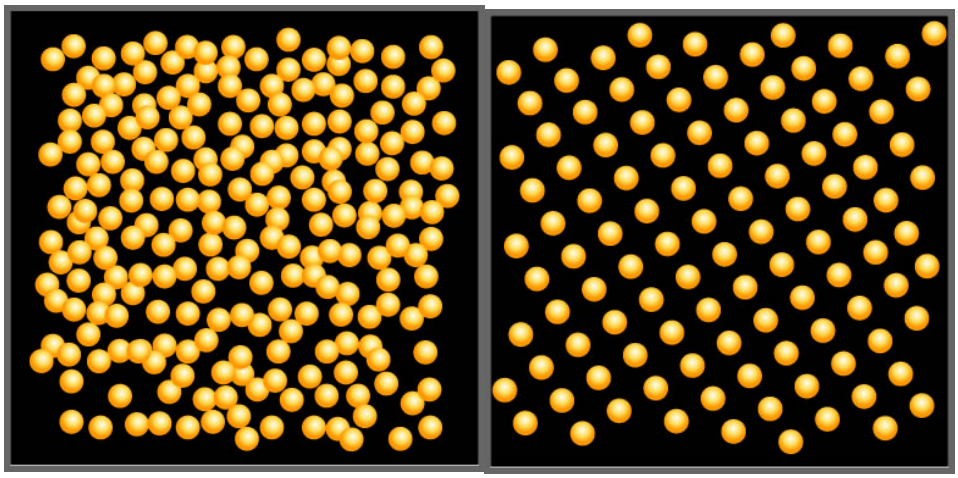
Crystallography is the science of determining the arrangement of atoms in solid matter. This science is important to the advancement of applied sciences and technologies, and material science. It provides information necessary for the development of metal and metal alloy structures, ceramics, glasses, and polymers. For micro and nanotechnologies, it provides information for the design and development of micro and nano-sized components.



Microcantilever Array
[Image courtesy of Dr. Christoph Gerber, Institute of Physics, University of Basel. This cantilever array was developed by the Cantilever Array Sensor Group at the Swiss Nanoscience Institute.]

The scanning electron microscope (SEM) image above shows a microcantilever array that was etched from a crystalline silicon substrate. The crystalline structure of silicon allows for the fabrication of micro-sized sensors such as these cantilevers that are strong, ultrasensitive, and fast-responding. Such sensors can be used in a variety of applications in chemistry, physics, biochemistry and medicine.[5]

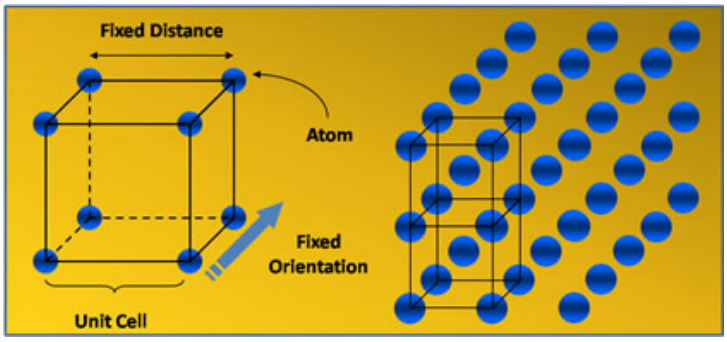
Solid Arrangements



Amorphous vs. Crystalline structures

Matter without a regular arrangement of atoms is called amorphous or non-crystalline. Matter composed of atoms arranged in a definitive pattern with a repeating structure is called a crystal. *(See illustrations above.)* Crystals consist of a repeating structure called a unit cell.

The Unit Cell



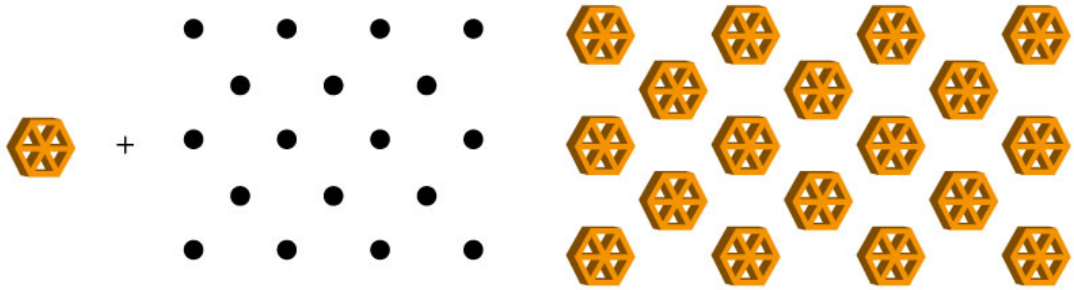
Unit Cell and Unit Cell configuration

The unit cell is the simplest repeating unit in a crystal. In a single crystal, all unit cells are identical and oriented the same way (fixed distance and fixed orientation). The opposite faces of a unit cell are parallel *(see graphic of unit cell)*. The edge of the unit cell connects equivalent points. The resulting structure is a lattice.

The figure above illustrates a unit cell for a crystalline structure.

The Lattice

The pattern of a crystal is like the repeating pattern on wallpaper. The motif is analogous to the unit cell and the arrangement of the motif over the surface is like the lattice.

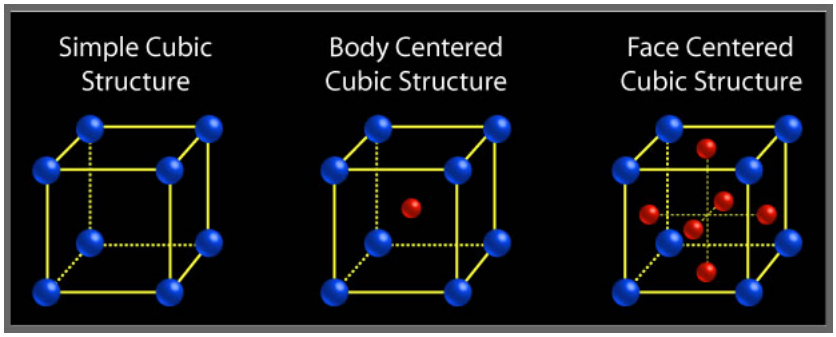


The lattice is a repetition of unit cells and when viewed from different angles or planes one would see different geometries or patterns.

Check out this 3D crystal viewer.[1] (http://www.dawgsdk.org/crystal/en/library/diamond) This applet allows you to move a crystal around so you can see it from different angles. (Select "Diamond" from the Archives list.)

All Unit Cells are Not Alike

There are several different configurations for unit cells. The simplest being the three configurations below.



The *Simple Cubic Structure* is a unit cell consisting of **one atom**. You are probably confused by that because you see eight atoms; however, remember that

- unit cells form a lattice and
- the edge of the unit cell connects to equivalent points.

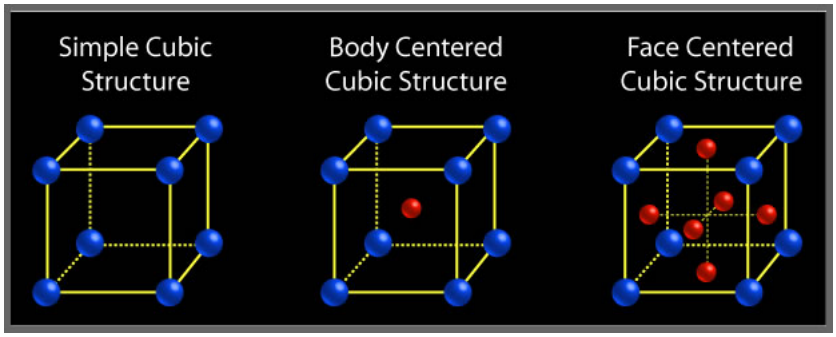
Therefore, each of the atoms you see in the *simple cubic structure* contributes ONLY 1/8 of itself to the unit cell. As the crystal structure forms, seven more unit cells bond with each of the eight atoms. To see this in action, watch an animation of how a body-centered cubic configuration forms a crystal.[2] (http://departments.kings.edu/chemlab/chemlab_v2/bcc.html) Pay close attention to how each corner cell bonds to other unit cells.

How many atoms are there

- ***in a "body centered cubic structure"?***
- ***in a "face centered cubic structure"?***

How many atoms are there in a "body centered cubic structure"? ***If you said TWO, you are correct!***

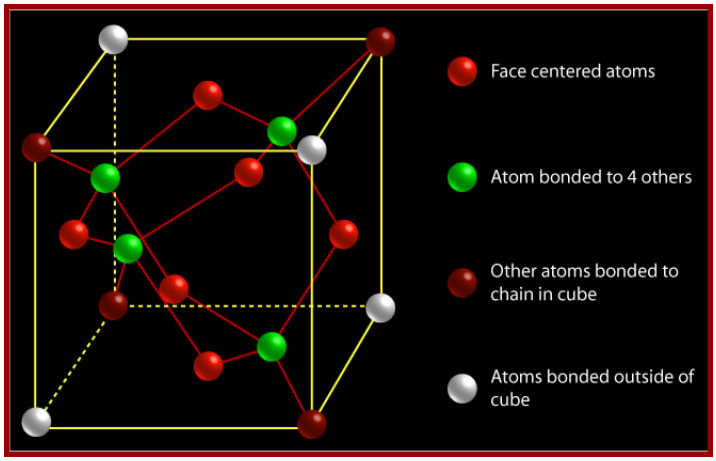
in a "face centered cubic structure"? ***If you said FOUR, you are correct!***



The body centered cubic has ONE atom from the eight corners, then the stand-alone atom on the middle: TWO atoms

The face centered cubic has ONE atom from the eight corners, then ONE-HALF an atom from *each of the face centered atoms:* 1 + ½ * 6 = 4

Carbon Unit Cell



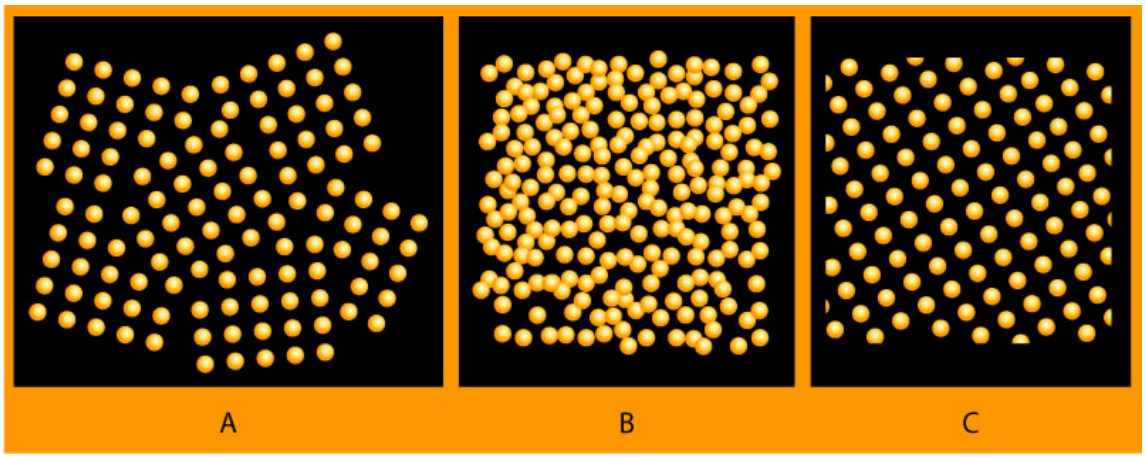
This is the unit cell for Silicon (Si), Germanium (Ge), and carbon (C). Identify the "face-centered atoms".

This unit cell can combine with other unit cells in a variety of ways. To see variety of structures formed by the carbon unit cell, Google ***Carbon structures*** and view "images". You should find structures such a carbon sheets, carbon nanotubes, bucky balls (also called fullerenes), and diamonds.

What's What?

Earlier, we talked about solids being a crystalline structure (e.g., diamond) or an amorphous structure (e.g., glass). However, not all crystal structures are alike. A true crystal or single crystal structure is one continuous crystal. Sometimes a crystal structure is made of many, single crystals. These are polycrystalline structures.

Which of the following graphics (a, b, or c) illustrates crystalline, polycrystalline or amorphous?



Correct answer:

a. polycrystalline
b. amorphous
c. crystalline

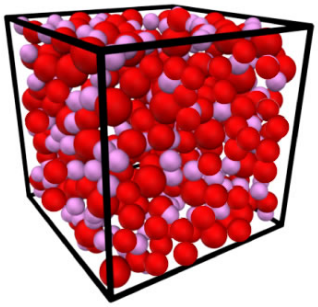
Let's take a closer look at the three arrangements.

Amorphous (Noncrystalline)

Question: What do you think of when you hear the word "amorphous"?

When a solid's atoms are randomly "arranged" in a non-predictable order, the solid is referred to as amorphous. Which of the following are amorphous solids?

- Styrofoam
- Window glass
- Salt
- Wax and paraffin
- The pattern of a tiled floor
- Peanut brittle



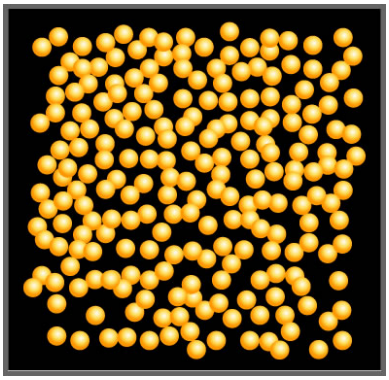
Amorphous solid structure of Silica Glass

If you said all but salt and a tiled floor, you are correct. When you break a piece of peanut brittle, it does not break along a straight edge. Instead it shatters into pieces of different sizes and different shapes. It shatters because it is amorphous, having no definitive edges.

Peanut Brittle

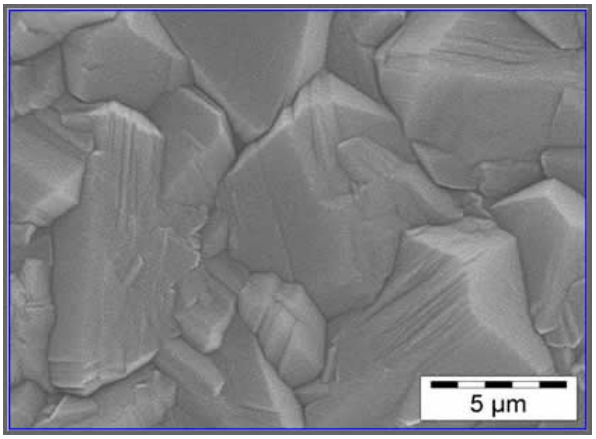
Amorphous solids have the following characteristics:

- No long range order exists at the atomic level. No predictability in the position of atoms, even over a short distance (i.e. a few nanometers).
- An amorphous solid cannot be cut (cleaved) like a crystal. It shatters rather than breaks along a plane.



Amorphous "arrangement"

Polycrystalline



Scanning electron microscope image of a polycrystalline carbon in a diamond structure.
[Courtesy of Prof. Dean Aslam, Michigan State University]

Crystalline structures are either single crystal or polycrystalline (poly being "many").
In both structures the atoms are arranged in a pattern consistent with the unit cell. Diamonds formed in nature are single crystal diamonds. However, polycrystalline diamonds (like the one shown above) are being fabricated for use in high temperature cutting tools, cell phones, and are being explored for use in "MEMS, high-frequency, high temperature and radiation hard device applications".[4] Some metals and metal alloys are polycrystalline. As like diamonds (carbon), silicon can be either polycrystalline or crystalline.

Grains

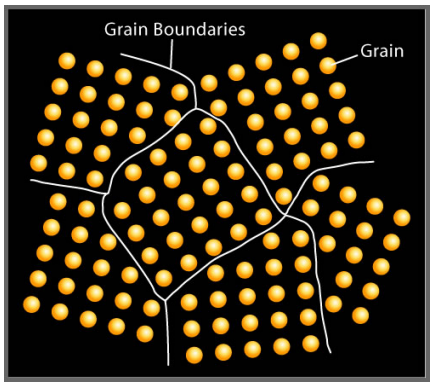
Polycrystalline materials are made up of a myriad of small individual crystal grains. The grains randomly arrange to form the final structure. In the photo, the individual grains of this polycrystalline mineral sample are clearly visible. Each *grain* is a small crystal.

Can you see how the grains connect to each other to form this polycrystalline structure?

In amorphous materials, the unit cells are randomly arranged throughout the material – random distances, random orientations. Grain crystals do not form.

Remember the peanut brittle and how it shattered?
How do you think polycrystalline material would break?

If you said that it would break according to the individual *grains*, you were correct! However, in polycrystalline material the grains are not aligned predictably to each other. In a mono-crystal, the entire solid is a single gigantic grain. In the figure of the polycrystalline material, note the "grain boundaries".



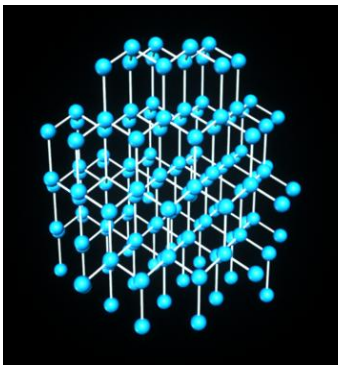
Polycrystalline structure showing grains and grain boundaries

Polycrystalline solids have the following characteristics:

- Long range order exists. Polycrystalline solids consist of crystal grains stuck together; Each crystal grain consists of billions and billions of atoms with predictable placement. Each grain is a mono-crystal.
- Polycrystalline solids do not shatter like amorphous solids. When broken, they tend to break along the grain boundaries (the boundaries form when individual grains are joined).

Based on these characteristics, what are some other examples of polycrystalline solids?

Crystals



Crystals are defined by a regular, well-ordered atomic lattice structure. A lattice consists of stacked planes of atoms. Because the atoms of the crystal fit together repeatedly and are held together by strong electrical attractions between each other, a crystal is typically very strong.

High quality diamonds found in jewelry consist of tight, dense carbon lattices as illustrated in this image of a diamond structure. The less compact the carbon lattices, the less valuable the diamond. Other crystal solids include gemstones, salt, sugar, some metals, pure silicon, and germanium.

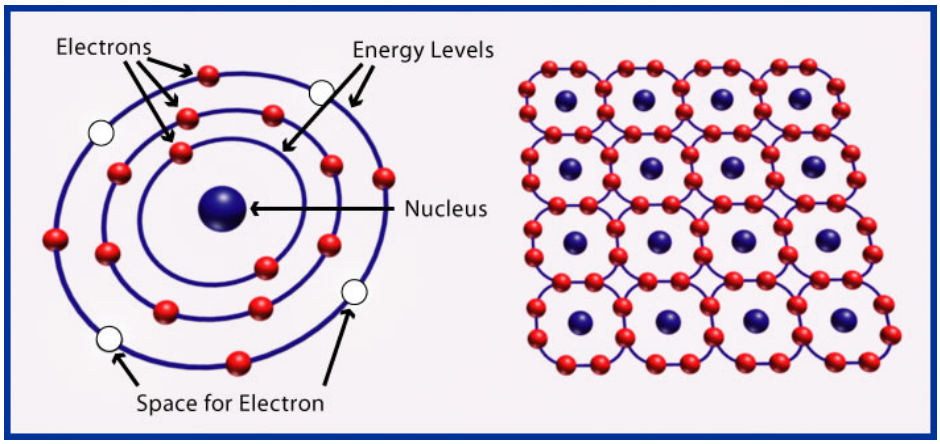
Crystals have the following characteristics:

- Extremely long range order and predictability exists with very few defects. If you could get inside a crystal, you could move from one end to the other and see no difference in the placement of the atoms. The environment is always the same throughout the crystal solid.
- Crystals can be cut along flat planes called cleavage faces. Cutting a crystal is essentially separating one lattice plane from its adjacent plane. This produces a near perfectly flat surface.

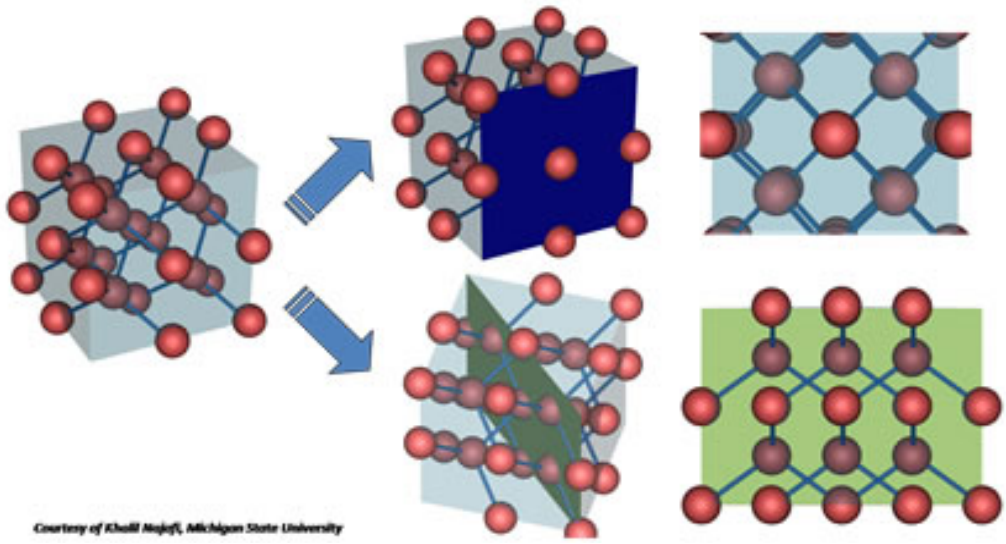
A Closer Look at the Silicon Crystal

Silicon crystal is widely used in micro and nanotechnologies. A silicon (Si) atom has four valence electrons that are *shared* with four other atoms to form four *covalent bonds* when forming a crystal. By sharing electrons this way, each atom's valence shell is complete. This results in solid matter that *is electrically stable* and a *poor conductor of heat.*

In the graphic below, notice that the outer energy level has four electrons and space for four more. On the right, you should see that **each silicon atom** is *bonded to* **four other silicon atoms.** In other words, each "electron space" is filled by one electron from one other silicon atom. The figure on the right is a two-dimensional crystal lattice or sheet.



The orientation of the silicon crystal denotes which crystal plane is exposed on the wafer surface. *(Refer to the graphic below for the following discussion).* The left most image is a silicon crystal. The middle images highlight two different planes within the silicon crystal. Think of looking at the same crystal from two different directions. The images on the right are what you would see looking at the face of each plane. Same crystal, same distance between unit cells, and same orientation of unit cells. However, looking at different planes, presents a different picture.



Silicon Crystal Planes
[Graphic courtesy of Khalil Najafi, University of Michigan]

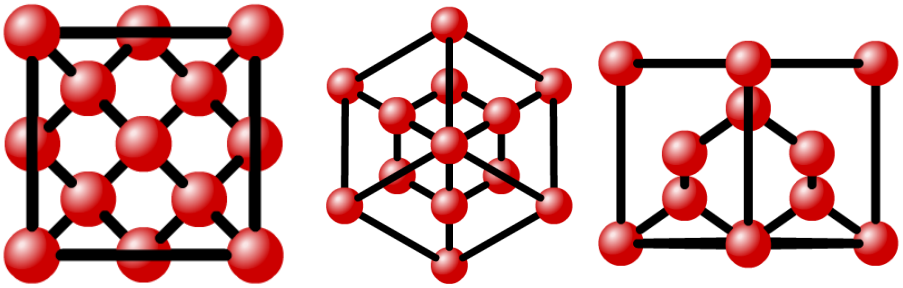
Silicon Properties

The surface properties of a silicon mono-crystalline wafer vary depending on the orientation of the lattice relative to the wafer surface. This orientation affects

- the properties of the wafer,
- the number of atoms on the wafer surface, and
- the wafer's conductivity (electronic properties) and reaction potential.

For example, the ability to etch silicon crystal in potassium hydroxide is dependent on this orientation (what arrangement is presented to the surface). Also, a silicon crystal has different bending (mechanical) properties depending on its orientation to applied stresses.

Count the number of atoms in the two plane faces shown above right. Revisit 3D crystal viewer[1]. It might help you understand this graphic better. Use the diamond as an example. Rotate the diamond unit cell to find each of the following planes.



Crystal Planes

Planes are the *second level or organization* in crystal structure. They describe the *orientation of the crystal*, which is dependent on the orientation of the individual unit cells within the crystal. Each type of plane is unique, differing in atom count and binding energies and therefore in chemical, electrical and physical properties.

The Miller Index helps us to identify crystal planes.

The Miller Index

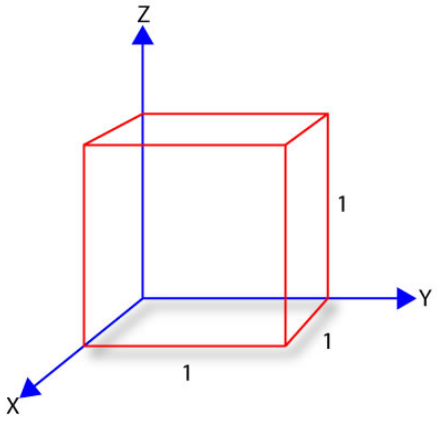
The Miller index is a roadmap or compass for identifying the crystal planes of crystals. Miller indices are three digit notations that indicate planes and direction within a crystal. These notations are based on the Cartesian coordinate system of x, y, and z. The Cartesian coordinate system is illustrated using the three vectors (axes) x, y, and z.

Referring to the graphic "*Cartesian Coordinates",* the

- x-axis vector is denoted [1,0,0]
- y-axis vector is denoted [0,1,0]
- z-axis vector is denoted [0,0,1]

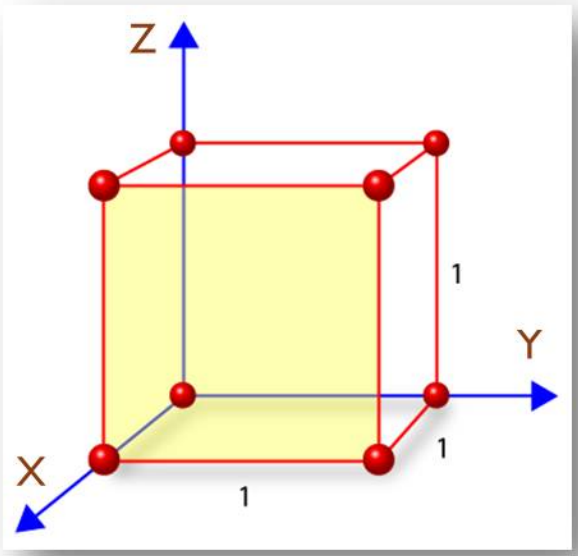
(Think of the "1" as being "1 unit" out from the origin or 0,0,0.)

Alternate vectors are indicated with < >, such as <100>, <010>, or <001>.



Cartesian Coordinates

Identifying the Crystal Plane



Crystal planes, each perpendicular to its respective vector (or axis: x,y,z)

Crystal planes are perpendicular to their corresponding axis. For example, the plane perpendicular to the [1,0,0] axis or x-axis, is the (1,0,0) plane (shown in the figure). Notice that the (100) plane is perpendicular to the X vector and parallel to the plane formed by the Y and Z axes. In a crystal there are an infinite number of (100) planes. To visualize this, think of each card in a deck of cards standing on end, perpendicular to the table top and parallel with all of the other cards in the deck.

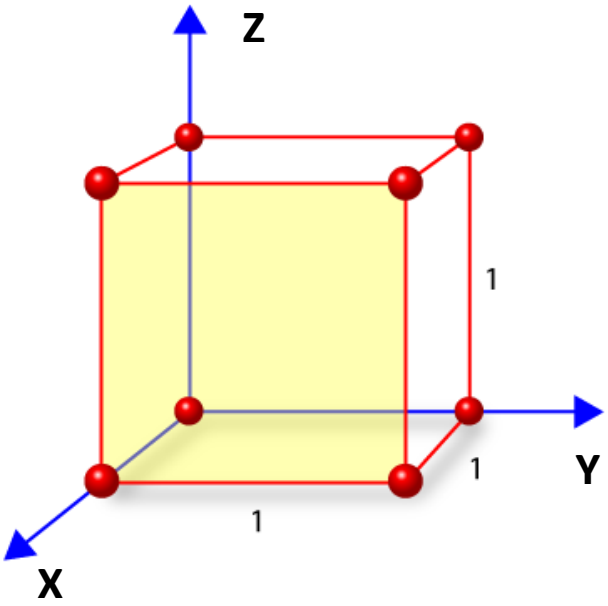
Each plane in a crystal structure has a unique notation and the notation depends on the plane's orientation.

- (1,0,0) or (100) is perpendicular to the x-axis
- (0,1,0) or (010) is perpendicular to the y-axis
- (0,0,1) or (001) is perpendicular to the z-axis

The above graphic illustrates a unit cell relative to the x-y-z axes and the yellow plane denoted (100).

Alternate planes are denoted using {}, such as {100}, {010} and {111}.

The (100) Plane

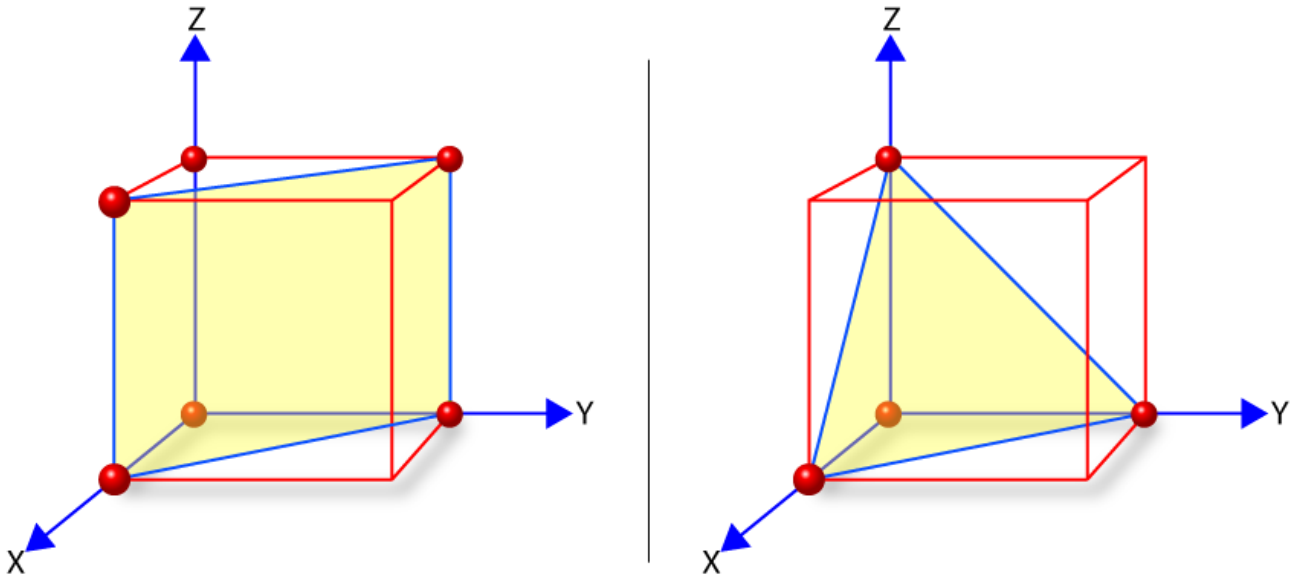


The (100) plane is perpendicular to the x-axis (x-vector), but parallel with the plane formed by the y and z axes. Can you see this in the graphic?

If not, start with the point at which the (100) plane touches the x-axis. Is the plane perpendicular to the x-axis?

Now move along the bottom edge of the plane toward the right. Is this edge parallel to the y-axis? You should now be able to see that the vertical edge of the (100) plane is parallel to the z-axis.

What's What?



What are the Miller indices for each of these planes?

Why is Crystal Orientation Important?

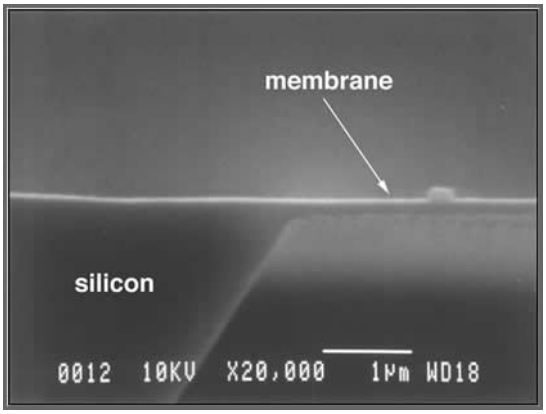
Microsystems consist of structures with defined edges, lengths, widths or thicknesses. They also require certain

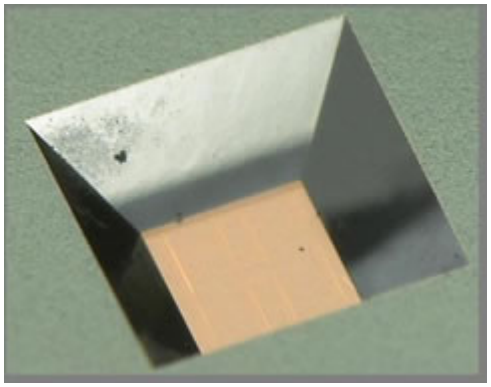
- electrical (e.g. resistance),
- mechanical (e.g. bulk modulus), and
- optical (Index of Refraction) properties.

Each of these properties can be different in different crystal orientations.

The structures in the Scanning Electron Microscopy (SEM) images below show a mono-crystalline silicon wafer that has been coasted with silicon nitride on both the front and back surfaces. The silicon nitride acts as a membrane on one side of the wafer and a hard mask on the other side of the wafer. The left image shows the membrane. In the right image, the membrane is the "brown" color and the hard mask is the "green" color on the top of the wafer. The openings in the hard mask allow one to etch through the silicon wafer to the membrane on the opposite side.

Note the sharp edges of the silicon. This was not accomplished by accident. A (100) silicon substrate and KOH (potassium hydroxide) etchant were used. The chemical reaction between the KOH and the silicon resulted in the anisotropic etch, the selective removal of material in one direction more than in another direction. The picture on the right shows the backside of a wafer.





(Left) Diaphragm (membrane) for MEMS pressure sensor over an etched silicon substrate [SEM courtesy of University of Michigan]

(Right) Backside view of the etched silicon crystal wafer. The green represents silicon nitride thin film (hard mask) on top of the silicon substrate while the gold (or brown) is a thin film of silicon nitride (membrane) on the opposite side of the wafer. *[Courtesy of the MTTC / University of New Mexico]*

By choosing specific wafer crystal orientation and etchant, one can create a multitude of different shaped structures:

- V-grooves
- Micro fluidic channels
- Cantilevers and bridges
- Mesas or pyramid shaped structures
- Cavities and holes

Determining the orientation

To determine the orientation of a silicon crystal wafer, crystallographers use x-rays aimed at a tiny piece of the wafer containing trillions of identical atoms. The specific periodic arrangement of the atoms within the crystal diffracts the x-rays onto an electronic detector or film. The resulting diffraction pattern on the film or detector gives the crystallographer the information needed to determine the actual orientation of the tiny seed crystal and the spacing of the atoms. A computer reconstructs the orientation from the diffraction pattern. The images below show the resulting patterns of three planes of a silicon crystal. Indicate which image represents each of the following planes. *(Think about the spacing of atoms and the number of atoms in different silicon planes.)*

a. (111)
b. (100)
c. (110)

Crystal orientation of three different planes of a silicon crystal.
X-ray was used to create these images.
[Images printed with permission and from the personal collection of Christopher C. Jones[3]]

As you can see, there is quite a bit of information in the patterns:

- Spacing between dots
- Relative orientations
- Angle between patterns and different dots

Such a pattern can be reconstructed into a 3-D image for a better view of the crystalline structure.

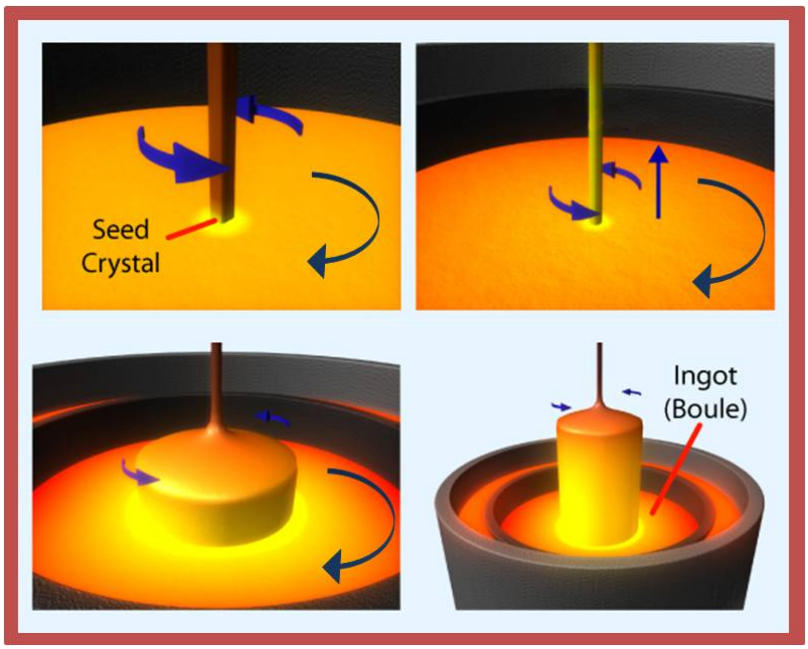
This same process is used to determine the double helix structure of DNA. Technicians crystallize the DNA, then put an x-ray beam through it. Because they have to use a weak x-ray beam, exposure time is long; however, eventually a diffraction pattern appears.

Answer: (100), (110) and (111), respectively (HINTS: The (100) pattern has fewer atoms and right angles are distinct in the pattern. The (111) pattern has the most atoms on the surface.)

Another method to determine the crystal orientation of a silicon wafer is to break it. Remember that a crystal is a lattice structure; therefore, when a silicon wafer breaks it will break along a lattice plane.

To see this for yourself, complete the SCME "Breaking Wafers Activity" which is part of this overall learning module.

Making a silicon wafer



The CZ (Czochralski) method of growing a silicon ingot

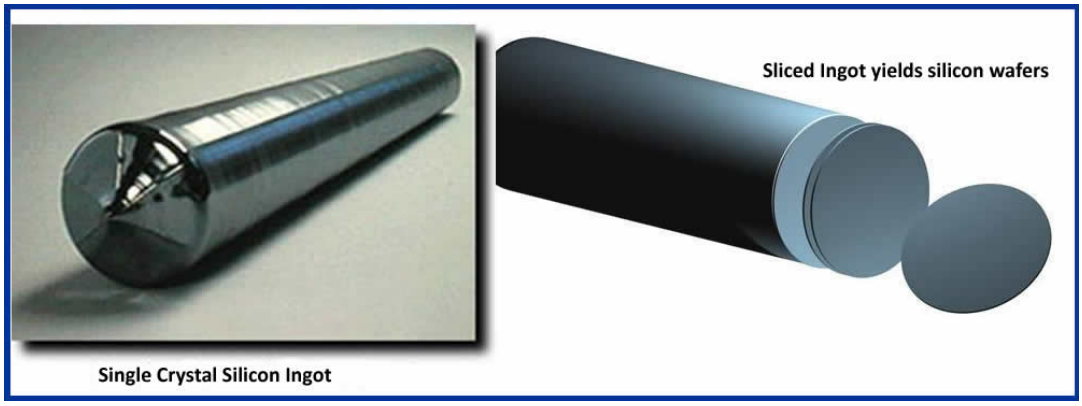
How is a silicon crystal formed and the orientation of a silicon wafer substrate determined?

1. First we start with very pure silicon material (99.999999999% pure!)
2. Melt the pure silicon in a crucible. (This molten silicon is called "the melt".)
3. Lower a seed crystal into the melt *(top left image)*. Silicon atoms in the melt align to the same crystal orientation. As the seed crystal is slowly pulled out of the melt, a large crystal ingot or boule is formed.
4. To "grow" this silicon crystal or ingot, rotate the seed and the crucible with the melt in opposite directions while slowly pulling the seed crystal upward.
5. The slower the "pull", the larger the diameter of the crystal ingot that forms. (This process is the Czochralski (CZ) Method of growing silicon.)

The seed crystal acts as a starting point for the alignment of the atoms in the molten silicon. The alignment of the seed crystal relative to the melt determines the orientation of the subsequently grown silicon crystal. The wafers cut from this crystal will maintain this orientation.

The Ingot

The resulting ingot is cylindrical in shape, 25.4 mm (~1 inch) to 450 mm (~18 inches) in diameter and several meters long. Once cooled, the ingot is ground to a perfect cylinder. The cylinder is sliced into thin wafers using diamond coated wires or saw blades. Each slice is polished to create silicon wafers, also referred to as substrates. Microsystems are constructed on or within these substrates depending upon the type of process used – surface or bulk, respectively.



Summary

Solid matter is either amorphous, polycrystalline or crystalline. Silicon polycrystalline wafers are widely used as the substrate for microsystems. These wafers provide the electrical and mechanical properties needed to build the components for electromechanical systems. Crystal orientations (100) and (111) are commonly used.

Food For Thought

Explain why the quality of a diamond is determined by its crystalline structure?

Why are only polycrystalline and crystalline materials used as substrates for microsystems components and devices?

Food for Thought / Answers

Explain why the quality of a diamond is determined by its crystalline structure?

Why are only polycrystalline and crystalline materials used as substrates for microsystems components and devices?

Glossary

Amorphous: Without order. Lacking definite form.

Band tailing: A characteristic that helps to define a material as being a conductor, insulator or semiconductor. Band tailing reduces band gap and increases conductivity.

Crystalline: A uniform arrangement of atoms / molecules in all directions.

Crystallography: The science of determining the arrangement of atoms in solid matter.

Grains: Small crystals. Grains are comprised of several unit cells of a crystal.

Grain Boundary: The edge formed by adjourning grains in a polycrystalline structure.

Miller Index: A notation system in crystallography for planes and directions in crystal lattices.

Miller indices: Three integers identifying a type of crystal plane.

Polycrystalline: Solid matter that is made of many smaller crystallites or grains with varying orientation. The variation in direction can be random or directed, possibly due to growth and processing conditions.

Unit cells: A unit of atoms arranged in a definite pattern with a repeating structure. A unit cell is a crystal.

References and Resources

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Support for this work was provided by the National Science Foundation's Advanced Technological Education (ATE) Program through Grants. For more learning modules related to microtechnology, visit the SCME website (http://scme-nm.org).