

Summary of the tutorials of Nanoscience and Nanotechnology – Ivo Meijers

Note: Topics handled in the lecture slides are not considered in this summary

Tutorial 1 – Fundamentals of nanomaterials

Definition of Nanomaterials:

According to the International Organization for Standardization (ISO) nanomaterial is defined as “a material with any external dimension in the nanoscale or having internal structure or surface in the nanoscale”. Nanoscale is in this definition defined as a length ranging from approximately 1 to 100 nm (nanometre).

Synthesis of nanomaterials:

The approaches to the synthesis of nanomaterials could be divided into two main classes:

1. Top-down approach

In top-down approach a greater bulk material is restructured to form nanomaterials. The top-down approach is applicable for greater devices and smaller and simpler component designs. Moreover, top-down assembly is difficult and expensive over large areas.

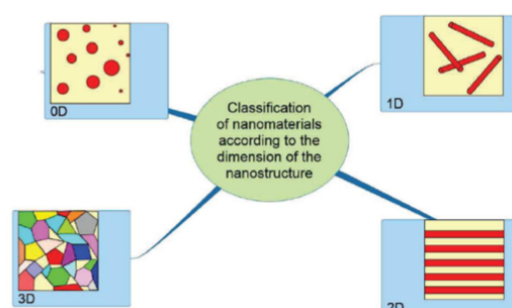
2. Bottom-up approach

In bottom-up approach nanomaterials are assembled from basic building blocks, such as molecules and nanoclusters. Bottom-up approaches is mostly applicable for small devices with complex component designs.

Classification of nanostructured materials:

Nanostructured materials can be distinguished by two different classes:

Dimensions - A material is a nanomaterial if *one dimension is less than 100 nm*. Therefore, a nano particle is 0-D if it has no dimensions larger than 100nm, if it has one dimensions larger than 100nm it is 1-D, a thin film is 2-D, and a three-dimensional structure (cubic) is considered as 3-D.



Composition – Nanomaterials could be classified on their composition in four different families:

1. **Carbon-based nanomaterials** – The nanomaterial is mainly composed by carbon.
2. **Metal-based nanomaterials** – The nanomaterial is made of metallic nanoparticles like gold, silver, and metal oxides (e.g., SiO_2 and TiO_2)
3. **Dendrimers** – Nanosized polymers built from branched units, which could capsule nanoparticles.
4. **Composite nanomaterials** – a mixture of simple nanoparticles or nano compounds.

Tutorial 2 & 3 - Quantum effects in nanomaterials

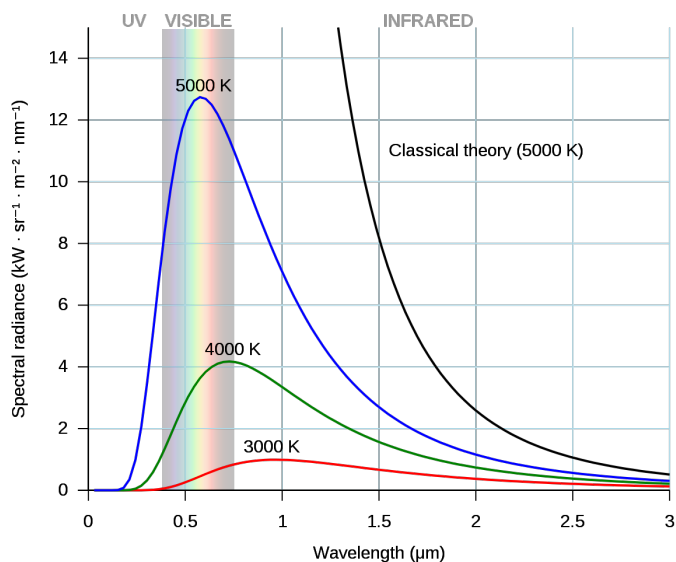
Freedom of electron delocalization:

The behaviour of bulk crystalline material changes when the dimension is reduced to the nanoscale.

- In 0-D there is no electron delocalization (freedom to move).
- In 1-D electron movement occurs in 2-D, so along the longer axis of the nanowire/rod/tube
- In 2-D the electrons are confined (limited) to the plane of the sheet, so electron movement will not occur in the thickness.
- In 3-D the electrons are fully delocalized.

Black body spectrum:

If a body perfectly absorbs light, then, when heated, the same body becomes the best possible emitter of thermal radiation. Ironically, the best possible emitter of light is also the best possible adsorber of light. This phenomenon is called a black body. For visible wavelengths (between 400 and 700 nm) the power of a black body is high, which could be translated in the amount of light an object emits. However, following this mathematical model, unlimited power (and therefore unlimited light) is predicted for objects with a very high temperature (in the graph shown as *Classical Theory*). This is known as the “ultra-violet catastrophe”.



Planck's hypothesis:

Planck postulated that the energy emitted by a black body is not continuous in nature. Instead, black bodies emit radiation in discrete packets (or quanta). When a vibrating atom changes its energy E_1 to a state of lower energy E_2 the discrete amount of energy (or quantum of radiation) $E_1 - E_2$ is equal to the product of the frequency of the radiation (ν) and the Planck's constant ($h = 6.62607015 \times 10^{-34} \text{ J*s}$). This relation is known as the Planck-Einstein relation:

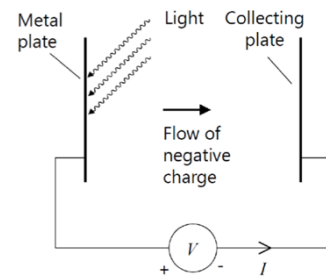
$$E_1 - E_2 = h * \nu = \frac{h * c}{\lambda}$$

Planck assumed that the sources of radiation are quanta (called *photons*) which oscillate to emit and absorb light and that these sources have a discrete series of value but never any value in between this series. The series of these energy values are given by:

$E = \left(n + \frac{1}{2}\right) hf$, where n is a non-negative integer and f is the frequency. This relation states that an atom can only increase or decrease its energy in discrete steps of size $\Delta E = hf$.

Photoelectric effect:

Hertz and Lenard found out that a flow of negative charge occurs from a metal plate to a collecting plate if they are in vacuum when a light is shone on the metal plate. Einstein showed that an electron comes loose from the metal plate (and thus a flow of negative charge is created) if the energy (depending on the velocity of the photon, $E_1 - E_2$) is high enough to overcome the *work function* ϕ_{met} . All the excess energy is taken up as kinetic energy. Note that here a particle with a mass, an *electron*, is emitted, while a massless particle, an *photon*, is absorbed. This is due to the fact that particles could act both as a wave and as a mass, see *wave-particle duality*.



Wave-particle duality:

Wave-particle duality states that light could act both as a wave and as a mass. In fact, every mass body has a wavelength. For an electron this wavelength is 10^{-10} m and for an average person this is about 10^{-37} m. For objects larger than a molecule, the wavelength is negligible. De Broglie found out that the wavelength of a body relates to the following equation:

$\lambda = \frac{h}{p} = \frac{h}{mv}$, where h is the Planck's constant and $p (=mv)$ the linear momentum.

For an electron in vacuum: $E = \frac{1}{2} m_0 * v^2 = \frac{3}{2} K * T$, in which m_0 is the mass of the electron, K is the Boltzmann-constant ($K = 1.380649 * 10^{-23}$ J/K) and T is the temperature. Plugging this in to the De Broglie wavelength equation, the following equation emerges:

$$\lambda = \frac{h}{\sqrt{3 * m_0 * K * T}}$$

For an electron at room temperature ($T = 300$ K): $\lambda = 6.24$ nm.

Hamiltonian:

Hamilton states that the total energy (both *kinetic* and *potential* energy) within a system will always stay the same, i.e. the change in total energy is zero. The total energy within a function is called the *Hamiltonian* and is given by:

$H = \frac{p^2}{2m} + V(r)$, where p is the linear momentum, m is the mass, and $V(r)$ is the conservative potential.

Type of waves:

1. **Classical waves** – all types of waves except the other described types in this list
2. **Helmholtz waves** – waves oscillating at one specific frequency ω (monochromatic)
3. **Standing waves** – the peak amplitude does not move in space

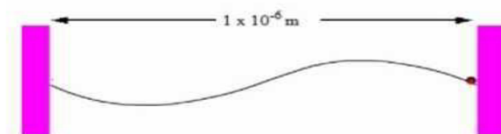
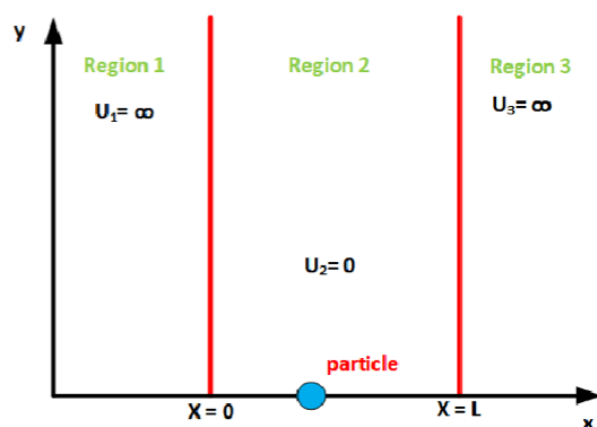
Schrödinger equation:

The Schrödinger equation predicts the position and the momentum of a quantum mechanical particle with a known mass. This equation could best be understood in its time-independent and 1-dimensional form which is given by:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) \psi(x) = E \psi(x)$$

This equation is an ordinary second-order differential equation and therefore it has the general solution: $\psi(x) = A \sin(kx) + B \cos(kx)$ in which A and B are arbitrary (complex) numbers and k is the wavenumber $k = \frac{2\pi}{\lambda}$.

An application of the Schrödinger equation is the “Particle in a box”. This box is a very small place which contains impenetrable walls on all sides. In classical systems, a particle can move at any speed and is no more likely to be found at one position than another. However, when this box becomes as small as the nanoscale, quantum effects will play a role. In this hypothetical example, the box has also impenetrable and infinity high walls and on both sides (left and right) the potential energy is infinite while within the box the potential energy is zero (space within the box is called the *well*). Now, the particle is so small that it will start to behave as a wave and will spread out over the whole box.



Tutorial 4 - Thin film deposition techniques (as opposed to thermal oxidation)

Deposition:

As an alternative to thermal oxidation, deposition is a method to create thin films as well. The two main ways of deposition are Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD).



Physical Vapor Deposition (PVD)

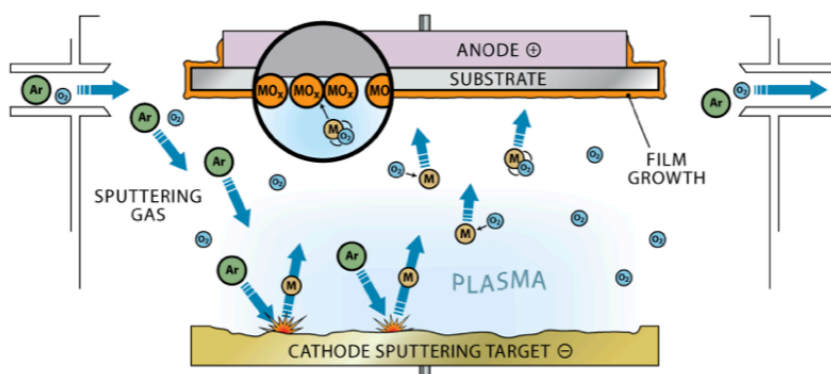
PVD could be distinguished in two different ways:

1. **Evaporation** – This method transfers atoms from a heated source to a substrate over a distance to form a film. Thermal energy is imparted to atoms, in a liquid or solid source, such that their temperature is raised to the point where they either evaporate or sublime.

Thermal evaporation – A solid material is heated in a vacuum chamber. The evaporated material forms a stream towards the substrate where it forms a film.

E-beam evaporation – Focused beam of electrons are used to locally heat the source material. This source material evaporates due to the high temperature. The evaporated atoms form a thin film on the substrate. *Advantages:* No contamination from crucible, high quality films, high deposition rate. *Disadvantages:* x-ray damage to the substrate, x-ray emission, expensive

2. **Sputtering** – Energized atoms are shot on a flat plate with a negative charge (called target). These energized atoms hit the target and propel negatively charged source material atoms off into the vacuum system. The substrate is positively charged by an anode. Therefore, these “sputtered off” negatively charged atoms travel to the substrate and there they form a thin film. *Advantages:* wider choice of materials, better adhesion, conformal coating, good controllable, useable for large wafers. *Disadvantages:* High costs, substrate gets heated.

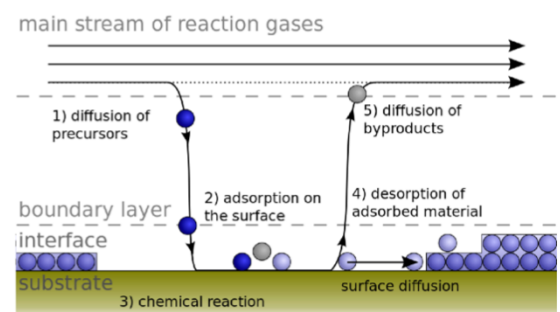


In general counts: Thermal evaporation for metals with a lower melting point, sputtering for metals with an average melting point and electron beam for metals with a high melting point.

If a thin film needs to be controlled precisely (in complex stoichiometries i.e., complex proportions of materials) or for metals with a very high melting point a laser could also be used. In this case a laser beam is shot at a source material and a small amount of material gets evaporated due to an extremely high temperature flash. This material is deposited onto the substrate without decomposition.

Chemical vapor deposition (CVD)

In CVD the substrate is heated while a precursor gas is streaming over its surface. Due to the high temperature a chemical reaction takes place at the surface. Over time more and more molecules are absorbed forming a film. All the by-products are transported away from the surface.



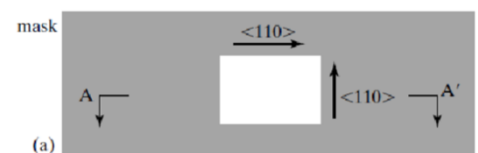
CVD could be distinguished into two classes:

1. **Based on their pressure conditions**
 - a. Atmospheric pressure CVD (AP-CVD) – used for polysilicon
 - b. Low Pressure CVD (LP-CVD) – used for polysilicon and silicon nitride
 - c. Ultra-High Vacuum CVD (UHV-CVD) (very low pressures) – used for silicon nitride, amorphous silicon, and silicon dioxide
2. **Based on their stimulus**
 - a. Plasma enhanced CVD (PE-CVD): energy from a high voltage through a plasma is used to create a reaction instead of temperature – used for substrate which cannot bare high temperatures
 - b. Photo-initiated CVD (PI-CVD): use of UV-light to create a reaction

Tutorial 5 – Silicon anisotropic wet etching

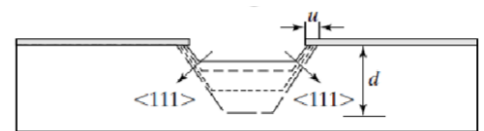
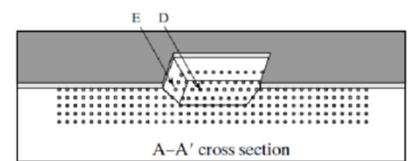
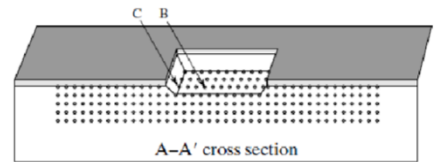
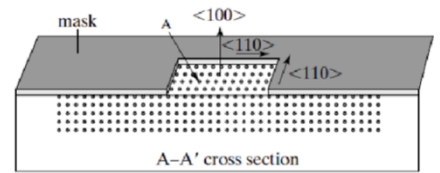
The simplest case of silicon anisotropic wet etching:

In the simplest case of silicon anisotropic wet etching there is made use of a mask with a square or rectangle opening (called window) upon a $\langle 100 \rangle$ oriented silicon substrate. The edges of the opening are aligned to the $\langle 110 \rangle$ direction. The outcome of the case is called the *self-limiting stable profile*. During the process it is called the *transitional profile*, which is called *unstable* if it happens fast and complex and *stable* if it occurs slowly and predictable.



The wet etching takes place according to the following steps:

1. Atoms on the top-most layer are closely packed and all face the $\langle 100 \rangle$ direction. A representative atom, atom A, can be removed according to the etch rate of the $\langle 100 \rangle$ direction.
2. Once the first layer is removed, the layer underneath that is exposed in the $\langle 100 \rangle$ and other directions. Only if an atom is surrounded by other $\langle 100 \rangle$ facing atoms on the same plane it could be attacked from the $\langle 100 \rangle$ direction. An atom on the edge of the carving, say atom C, has a greater bond strength than atom B, since it is flanked by $\langle 111 \rangle$ facing atoms. Therefore, the outer section of the layer is hardly etched.
3. As you move further through the layers, the number of $\langle 100 \rangle$ facing atoms flanked by $\langle 100 \rangle$ facing atoms (atom D) decrease, since the area becomes smaller. The atoms in the slope (atom E) are barely etched, since they are all $\langle 111 \rangle$ facing atoms.
4. As the etching process progresses, the vertical axis is etched by the etching rate in the $\langle 100 \rangle$ direction while the horizontal axis is etched by the etch rate of the $\langle 111 \rangle$ direction (almost negligible regarding to the etch rate of the $\langle 100 \rangle$ direction).

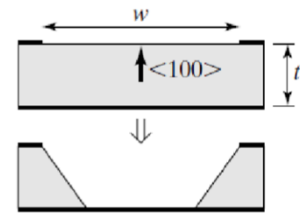


Therefore, the etching is working towards a *perfect point* in a square opening in the mask or towards a *knife-edge* in a rectangular opening in the mask. There is no undercut if we assume that the etch rate on $\langle 111 \rangle$ surfaces are negligible. If such a profile is completely through the wafer it is called a *through-wafer* hole. If it precisely reaches the end or stops before the wafers ends, it is called a *blind cavity*. The etching could be stopped using an *etch stop*.

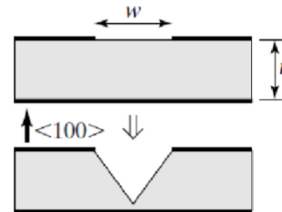
The angle between the $\langle 111 \rangle$ and $\langle 100 \rangle$ surfaces are always 54.7° . Therefore (simply by the Pythagoras law) the width of the window (w) and the final etching depth are related as follows: $d = \frac{w}{2} \tan 54.7^\circ$.

For any profile in which $T \geq \frac{t}{r_{\langle 100 \rangle}}$ (T = time, t = thickness, $r_{\langle 100 \rangle}$ = etch rate in the $\langle 100 \rangle$ direction) the following counts:

If $w > \frac{2t}{\tan(54.7^\circ)}$ then the SLSP profile is a through-wafer hole.

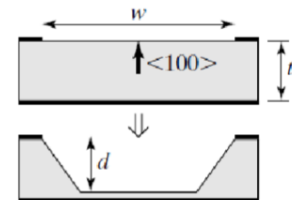


If $w \leq \frac{2t}{\tan(54.7^\circ)}$ then the SLSP profile is a blind cavity ending at a point or at a line.

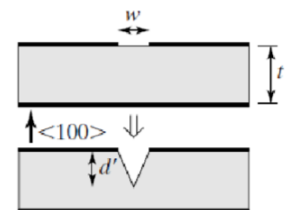


For any profile in which $T < \frac{t}{r_{\langle 100 \rangle}}$ (T = time, t = thickness, $r_{\langle 100 \rangle}$ = etch rate in the $\langle 100 \rangle$ direction) the following counts:

If $w > \frac{2T \cdot r_{\langle 100 \rangle}}{\tan(54.7^\circ)}$ then the SLSP profile is a blind cavity ending on a plane.



If $w \leq \frac{2T \cdot r_{\langle 100 \rangle}}{\tan(54.7^\circ)}$ then the SLSP profile is a blind cavity ending on a point or a line.



Complex cases in anisotropic wet etching:

Firstly, in complex cases the opening of a window is not an uninterrupted straight line. Moreover, there is no restriction that the edges must be parallel to $\langle 110 \rangle$ directions. In the window there are two types of corners: (i) *convex corners* – the solid angle is less than 180° and (ii) *concave corners* – the solid angle is greater than 180° . In convex corners undercut occurs, whereas in concave corners slow etching planes (such as $\langle 111 \rangle$) start to develop.

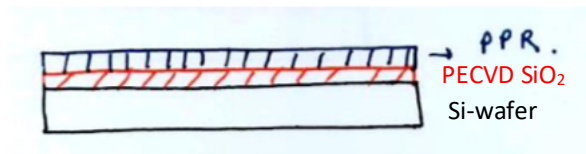
Tutorial 6 – Fabrication flow of simple MEMS structure

Cantilevers:

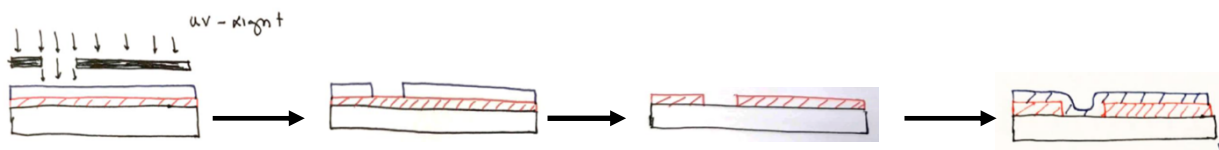
Microcantilevers (or MEMS cantilevers) is a widely used component in microsystem devices, such as sensors, switches and needles. They could be used for applications like detecting certain particles, to penetrate tissue, as grippers for picking and as a transport mechanism for sensors. Cantilevers are made from different materials such as, silicon, silicon nitride and polymers, depending on the operational requirements.

The fabrication of a cantilever:

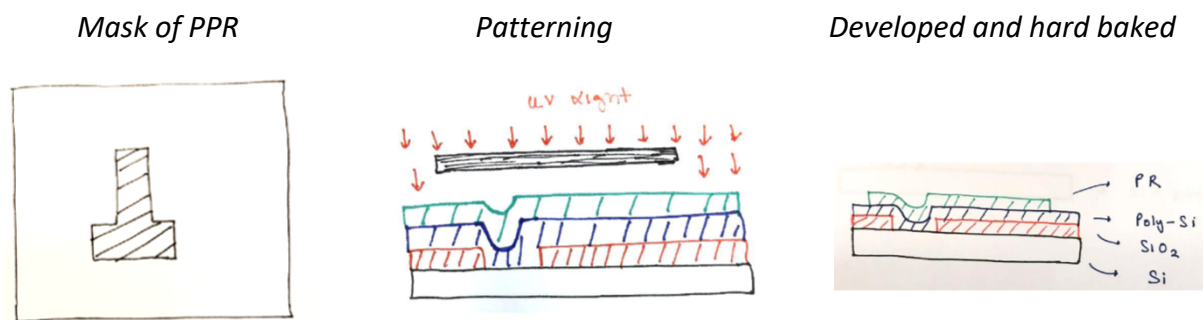
The starting point is a blank silicon wafer. On this wafer a silicon dioxide layer is placed through PECVD, which acts as a sacrificial layer. A spin coat positive photoresist for patterning and etching is put on top of that.



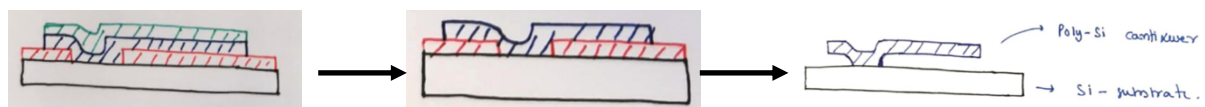
An appropriate mask for patterning the PPR is chosen. In this case it is a dark field mask. Using UV lithography a hole in the photoresist is made, after which it is hard baked. By etching the pattern is etched to the SiO₂-layer. Then, a polysilicon layer is deposited on the SiO₂-layer by LPCVD



Using a new mask and a new layer of photoresist, a new layer is added.



Then etching (either dry or wet) is applied to pattern the polysilicon. Thereafter, the leftover resist is stripped using removal solution. Finally, the sacrificial SiO₂-layer is removed by etching to obtain the desired end product, the cantilever.



Note: stiction (the friction which prevents stationary surfaces from being set in motion) is a serious problem when creating cantilevers. With this issue could be coped by incorporate it in the design or supercritical drying is used where the liquid is evaporated, which is without surface tension.

Other simple MEMS structures:

Pressure sensor – Two of the most common sensing mechanisms are piezoresistive and capacitive. These sensor could be used for example in blood pressure monitoring. The fabrication steps are extensively elaborated in the tutorial slides.

Capacitive accelerometer – capacitive accelerometers are devices that measure acceleration based on a change in capacitance due to a moving plate or sensing element. The fabrication steps are in the tutorial slides as well.