



Course material

Course:

Micro and Nanofabrication (MEMS)

Video:

6.4 Wet etching 4

Concepts (extracted from automatically generated subtitles):

Anisotropic etching of silicon. Crystal planes. Silicon wafer. Etching baths. Etching phenomena. Basis vectors. $\langle 111 \rangle$ -axis. Silicon atom. Different plane orientations. Different planes. Real space. Etching mechanism. Scale of the wafer. Hydroxyl ions. Etching rates.



[to video sequence search](#)
(within Micro and Nanofabrication (MEMS).)



[to video](#)

Center for Digital Education. More educational support material here:

<https://www.epfl.ch/education/educational-initiatives/cede/educational-technologies-gallery/boocs-en/>



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notes

summary

0m 0s





- Si crystal structure
- Etching mechanism
- Etching baths

Micro and Nanofabrication (MIM)

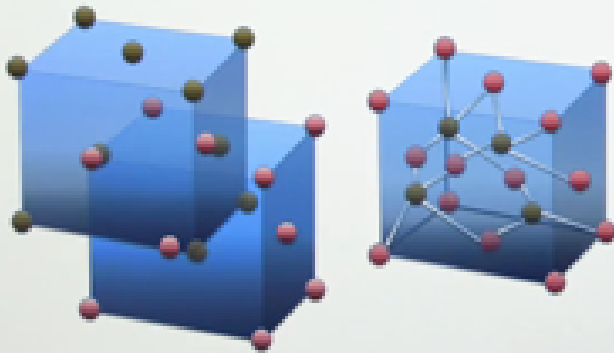
In this lesson, we will explain the anisotropic etching of silicon

notes

summary

0m 1s





- Si has the crystal structure of the diamond lattice and can be represented by two interpenetrating face-centred cubic lattices
- A Si atom forms four covalent bonds which are part of tetrahedrons
- Packing density and bonding strength of atoms in different plane orientations is different
- This can give rise to plane-dependent etching rates

Micro and Nanofabrication (MNF)

by which certain crystal planes will be chemically attacked by an etchant, while other planes will not react. These etching phenomena are observable because the silicon wafer is essentially single crystalline, that is, it has an ordered lattice structure on the scale of the wafer. We will explain the etching mechanism and some of the etching baths that can be used.

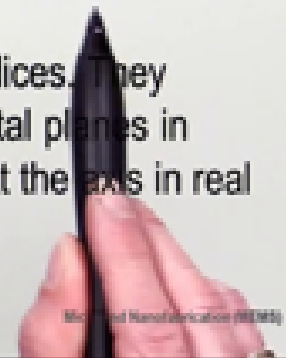
notes

summary

0m 5s



- Cubic crystal unit cell has three basis vectors with magnitude $a_x=ae_x$, $a_y=ae_y$, and $a_z=ae_z$ ($a=5.43 \text{ \AA}$ for Si)
- **Directions in real space**
Example: vector $r = 2e_x + 4e_y + 0e_z$ is characterised by direction $[120]$ (or $[240]$)
Directions $[100]$, $[010]$ and $[001]$ are crystallographically equivalent: they form the group of $\langle 100 \rangle$ directions
- **Crystal planes** are characterised by sets of three Miller indices. They describe vectors in the reciprocal lattice, normal to the crystal planes in question, and are the inverse of the intercept of the plane at the axis in real space



These drawings illustrate the silicon crystal structure which is that of a diamond lattice and can be represented by two interpenetrating face-centered cubic lattices. A silicon atom forms four covalent bond with other silicon atoms. If one cuts the silicon crystal along different planes, one will see that the packing density of atoms and the bonding strength between silicon atoms on different plane orientations is different. And this gives rise to etching rates that can depend on the plane orientation. A cubic crystal unit cell has three basis vectors and every point in real space can be written as the coordinate of a vector written in function of the three basis vectors. A real space coordinate or vector can be represented by three numbers as put in between the square brackets. So this direction is the same as this direction, only the vector here is shorter by a factor of two. In the crystal, the directions $[100]$, $[010]$ and $[001]$ are crystallographically equivalent. One is along a different axis but for the environment of the silicon atom,

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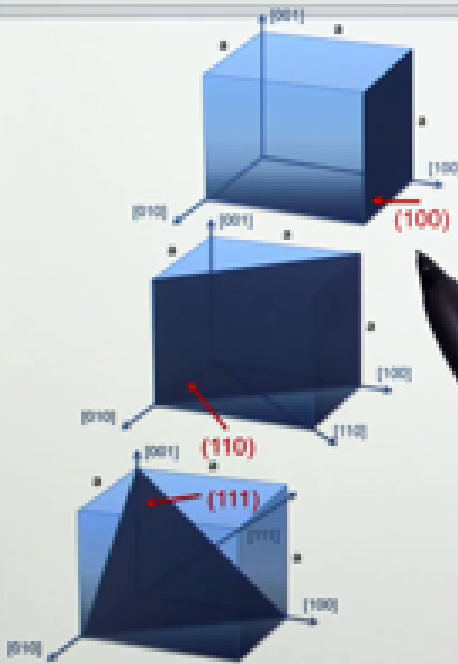
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summary

0m 36s





- A plane with Miller indices (hkl) is normal to the reciprocal lattice vector $hi_x + kj_y + li_z$.
- A plane with normal $(4-21)$ - or with cubic axis intercept $(1, -2, 4)$ -, is called a $(1 \frac{-1}{2} \frac{1}{4})$ or better $(4-21)$ plane
- Example 1: the plane (100) is normal to the vector i_x .
- Example 2: the plane (110) is normal to the vector $i_x + i_y$.
- Example 3: the plane (111) is normal to the vector $i_x + i_y + i_z$.
- The planes (001) , (010) , (100) , $(00-1)$, $(0-10)$ and (-100) are equivalent and marked as the $\{100\}$ family of planes.

Micro and Nanofabrication (MIM)

there is no difference. If one wants to speak of all these directions, together, one puts 1 0 0 with these triangular brackets: $\langle 100 \rangle$. In micro-fabrication, we are not so much interested in knowing the real space coordinate of each atom, but rather, we would like to know how the crystal planes are oriented in the wafer. A crystal plane can be characterized by three so-called *Miller indices* which describe a vector in the so-called *reciprocal space* that is normal to the crystal plane. The Miller indices are defined by taking the inverse of the intercept of the plane at each axis in real space, and we illustrate that now in the following. A plane with Miller indices (hkl) , and we use here now rounded brackets because it's a plane, is normal to this reciprocal lattice vector where these are the basis vectors of the reciprocal lattice, these three. A plane with a normal $(4-21)$, means that the plane intercepts the three cubic axes at 1, -2 and 4. Indeed, if we invert 1, -2 and 4, we obtain this reciprocal lattice vector and as one likes better whole numbers, one multiplies this vector by 4 to get this vector. By this operation, the orientation of the vector does not change, so it's the same plane. As we already pointed out, a reciprocal space vector is denoted by the rounded brackets.

notes

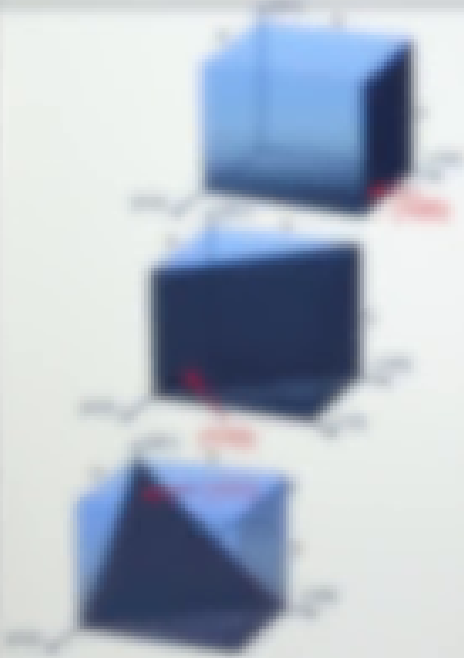
summary

2m 13s



Angle between crystal planes

EPFL



- As planes are characterized by vectors (of the reciprocal lattice), the angle between two planes can be calculated using the vector *in-product*

$$\vec{A} \cdot \vec{B} = |\vec{A}| |\vec{B}| \cos \varphi$$

- Example: angle φ between the planes (111) and (101)

$$\cos \varphi = \frac{(1 \ 1 \ 1) \cdot (1 \ 0 \ 1)}{\sqrt{1^2 + 1^2 + 1^2} \sqrt{1^2 + 0^2 + 1^2}} = \cos \varphi = \frac{1}{\sqrt{3} \sqrt{2}} = 54.74^\circ$$

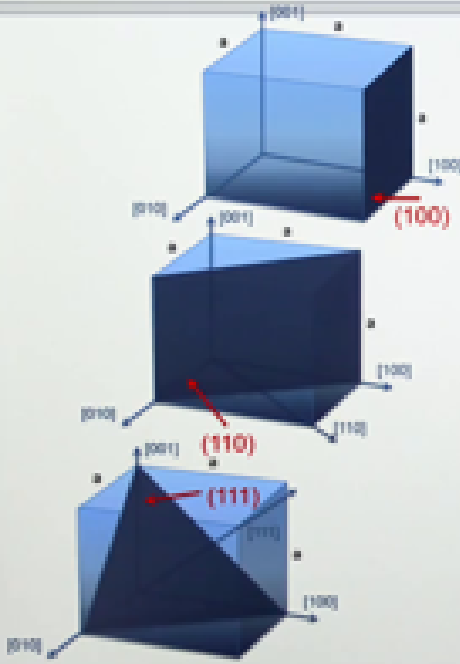
The upper drawing illustrates the position of a (100) plane which intersects the x-axis at 1, and the y and z-axis at infinity. So if we invert these, we get (100). The planes (001), (010), (100), and so on are equivalent, and if you want to speak of all of them together, we write it with these brackets: {100}. So this means this is the family of identical planes. In the same way, the drawing in the middle indicates the (110) plane. And the drawing below, the (111) plane. So this intersects, for example, each axis at one.

notes

summary

4m 25s





- As planes are characterized by vectors (of the reciprocal lattice), the angle between two planes can be calculated using the vector in-product

$$\mathbf{A} \cdot \mathbf{B} = |\mathbf{A}| |\mathbf{B}| \cos \varphi$$

- Example: angle φ between the planes (111) and (001) is

$$\arccos \left\{ \frac{(111) \cdot (001)}{|(111)| \times |(001)|} \right\} = \arccos \left\{ \frac{1}{\sqrt{3} \times 1} \right\} = 54.74^\circ$$

Micro and Nanofabrication (MNF)

As planes are characterized by vectors of the reciprocal lattice, one can simply calculate the angle between two planes by calculating the vector inner product; this product. And as an example, the angle ϕ

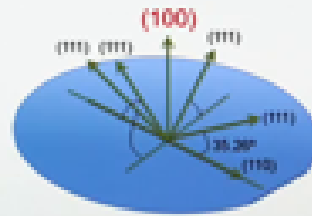
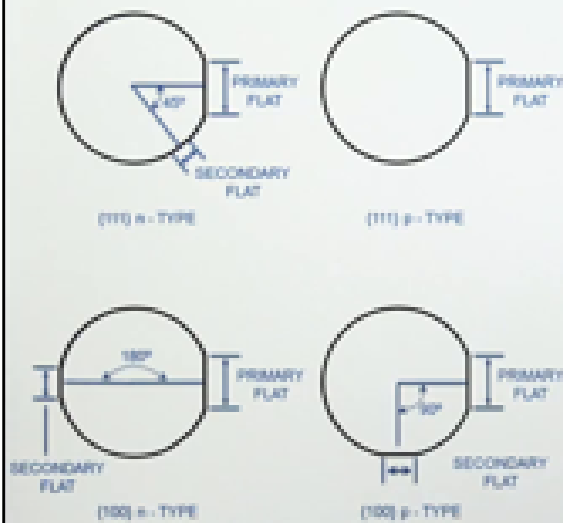
notes

summary

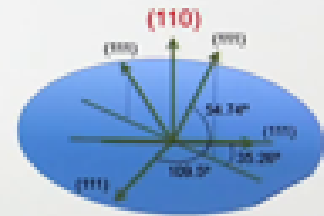
5m 21s



Orientation of wafer planes and wafer doping can be distinguished from the wafer flats



(111) planes of a (100) oriented wafer



(111) planes of a (110) oriented wafer

Micro and Nanofabrication (MEMS)

between the planes (111) and (001), is 54.74 degrees.

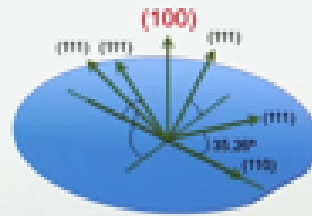
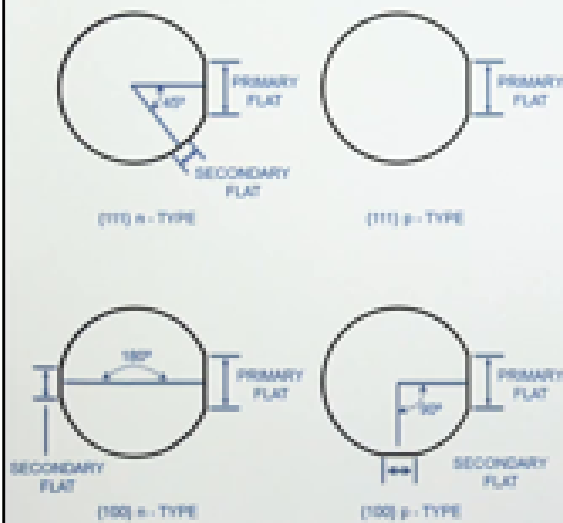
notes

summary

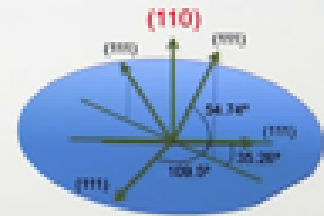
5m 37s



Orientation of wafer planes and wafer doping can be distinguished from the wafer flats



(111) planes of a (100) oriented wafer



(111) planes of a (110) oriented wafer

Micro and Nanofabrication (MNM)

If one has in mind a cubic crystal structure,

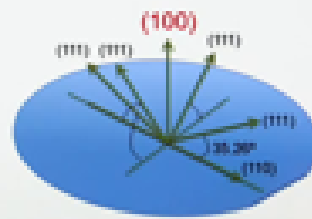
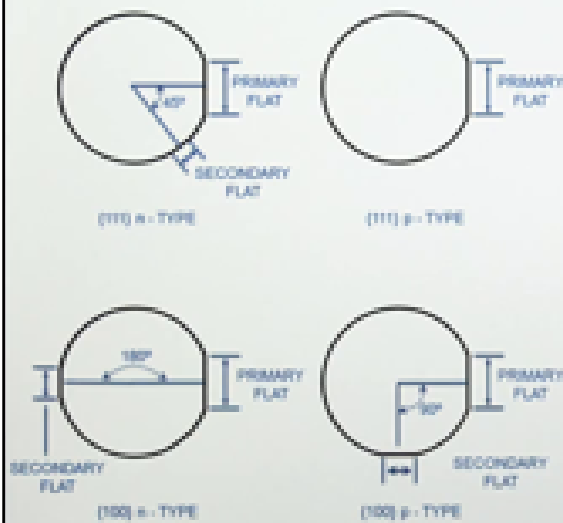
notes

summary

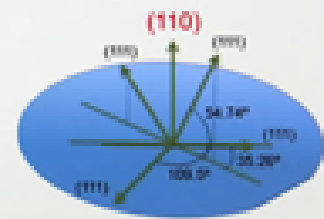
5m 49s



Orientation of wafer planes and wafer doping can be distinguished from the wafer flats



(111) planes of a (100) oriented wafer



(111) planes of a (110) oriented wafer

Micro and Nanofabrication (MEMS)

one can know the orientation of the different planes. For example, if the surface of the wafer has a (100) orientation, there are four (111) planes

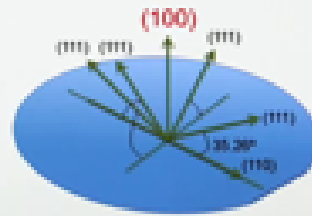
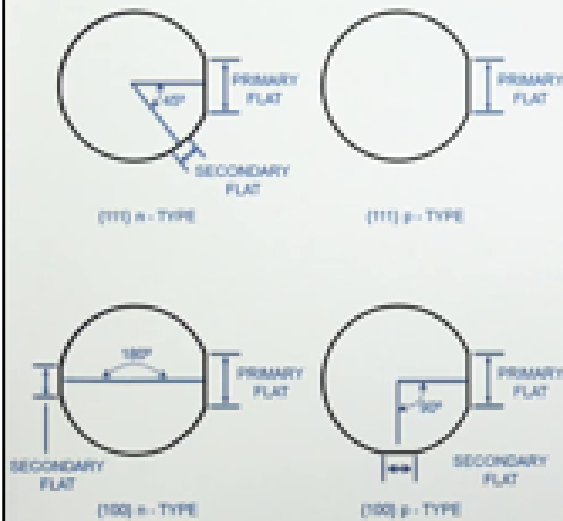
notes

summary

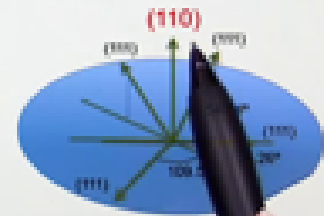
5m 55s



Orientation of wafer planes and wafer doping can be distinguished from the wafer flats



(111) planes of a
(100) oriented wafer



(111) planes of a
(110) oriented wafer

Micro and Nanofabrication (EPFL)

that have each an angle of 54.74 degrees with the plane of the wafer.

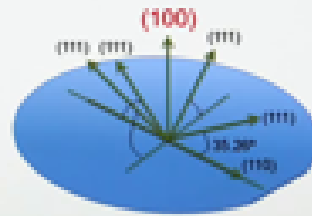
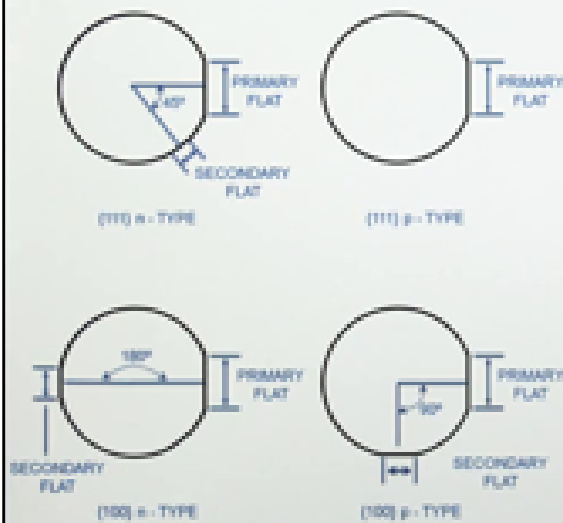
notes

summary

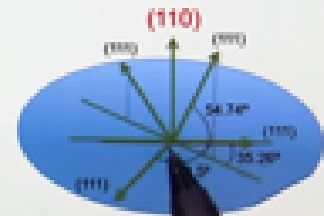
6m 12s



Orientation of wafer planes and wafer doping can be distinguished from the wafer flats



(111) planes of a (100) oriented wafer



(111) planes of a (110) oriented wafer

Micro and Nanofabrication (EPFL)

If the wafer has been cut from a crystal that had a (110) orientation, two (111) directions are now pointing outside of the wafer

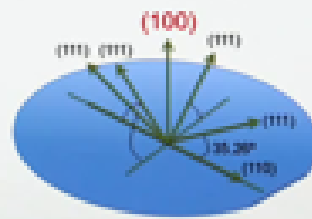
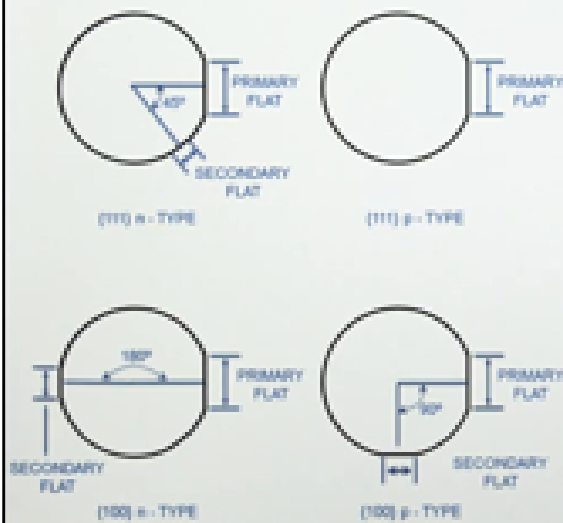
notes

summary

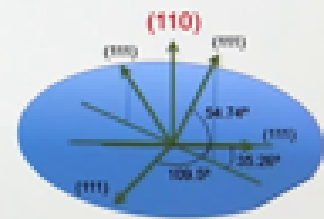
6m 21s



Orientation of wafer planes and wafer doping can be distinguished from the wafer flats



(111) planes of a (100) oriented wafer



(111) planes of a (110) oriented wafer

Micro and Nanofabrication (MNM)

and two (111) directions are inside. That means in this case, the (111) plane is vertical. There are two vertical (111) planes for a (110) oriented wafer.

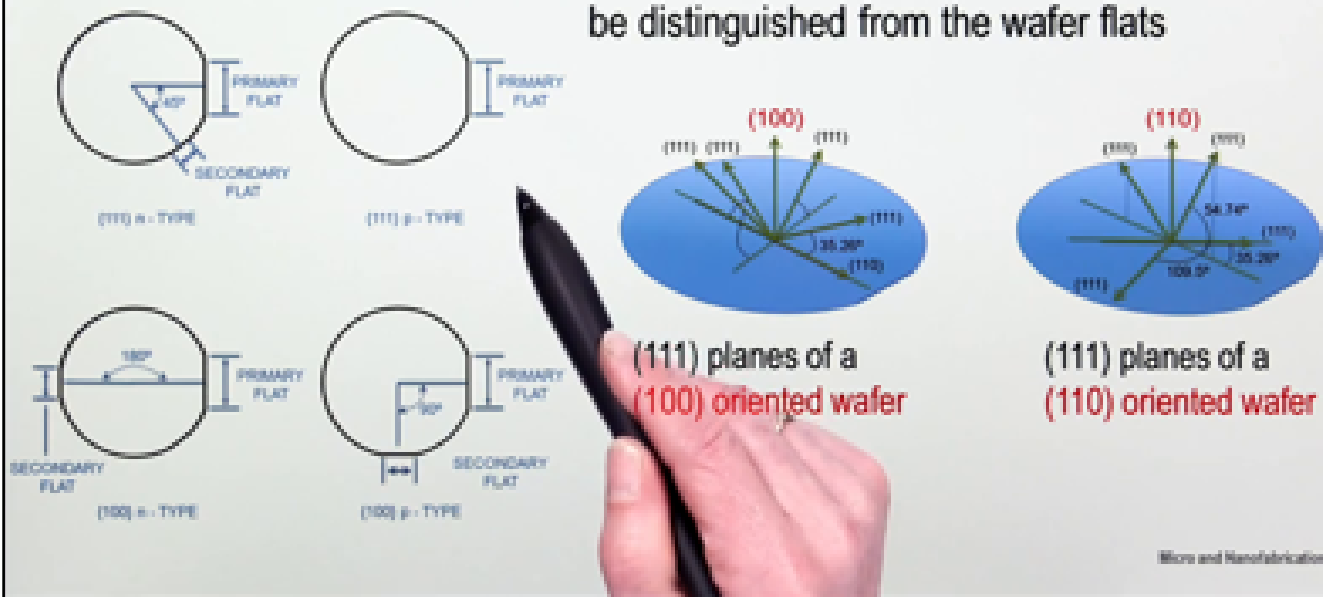
notes

summary

6m 31s



Orientation of wafer planes and wafer doping can be distinguished from the wafer flats



In practice, wafers have so-called *flats*: a primary flat and a secondary flat. Here, there's only a primary flat.

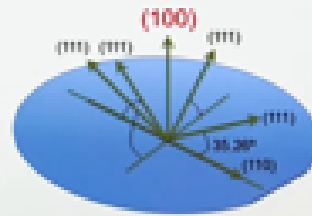
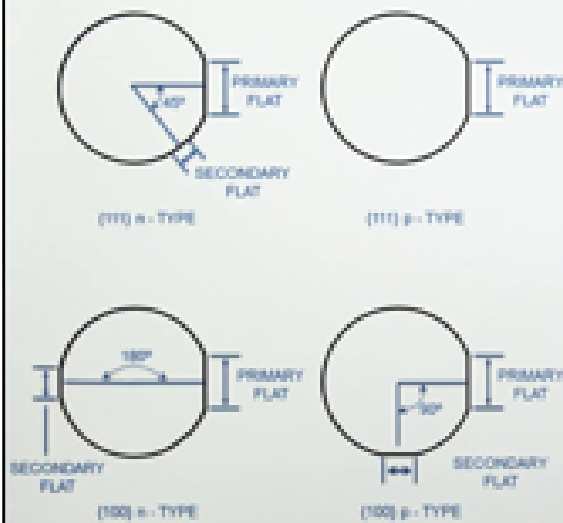
notes

summary

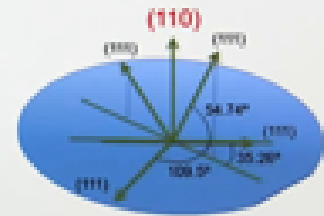
6m 49s



Orientation of wafer planes and wafer doping can be distinguished from the wafer flats



(111) planes of a (100) oriented wafer



(111) planes of a (110) oriented wafer

Micro and Nanofabrication (MNM)

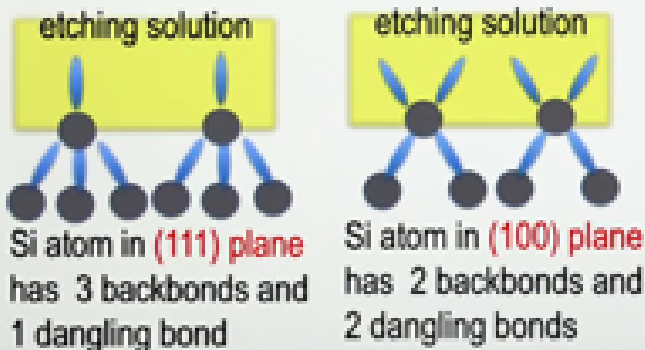
If you see a wafer, in principle you know

notes

summary

7m 0s





- A Si atom located in a certain plane is differently 'anchored' to the back of the substrate and has a different number of dangling bonds that are in contact with the etching solution
- This can give rise to plane-dependent etching rates
- Example: a (111) plane will etch much slower than a (100) plane in an alkaline etching bath

Micro and Nanofabrication (MNM)

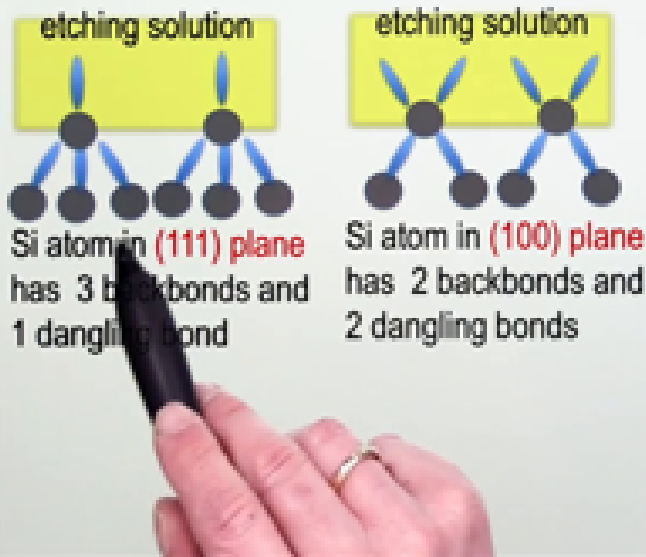
by looking at the flats what is the type of orientation of the wafer. So here is the orientation and here is the (100) orientation, and also you know the type of doping in the wafer by looking at the flats.

notes

summary

7m 2s





- A Si atom located in a certain plane is differently 'anchored' to the back of the substrate and has a different number of dangling bonds that are in contact with the etching solution
- This can give rise to plane-dependent etching rates
- Example: a (111) plane will etch much slower than a (100) plane in an alkaline etching bath

Micro and Nanofabrication (MNF)

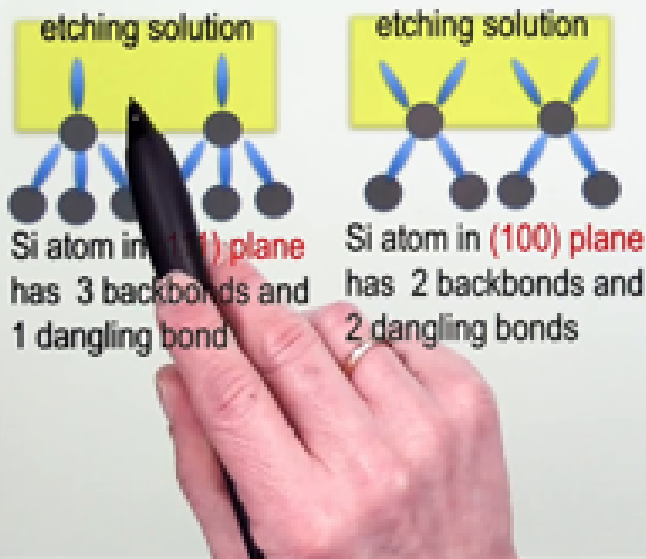
The reason why an etching bath preferentially attacks a certain lattice plane, and does not etch another plane is illustrated here. A silicon atom that is present in a (111) plane

notes

summary

7m 21s





- A Si atom located in a certain plane is differently 'anchored' to the back of the substrate and has a different number of dangling bonds that are in contact with the etching solution
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- Example: a (111) plane will etch much slower than a (100) plane in an alkaline etching bath

Micro and Nanofabrication (MNF)

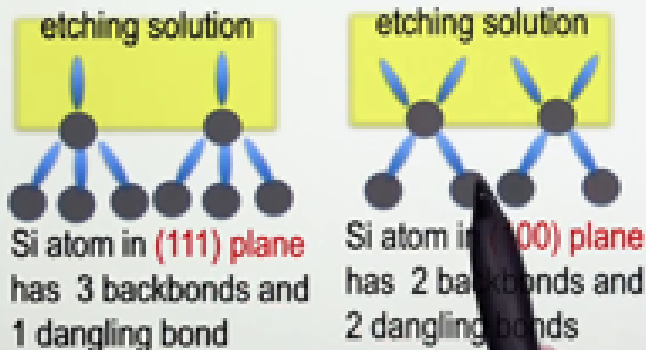
has three backbonds to the interior of the silicon wafer

notes

summary

7m 37s





- A Si atom located in a certain plane is differently 'anchored' to the back of the substrate and has a different number of dangling bonds that are in contact with the etching solution
- This can give rise to plane-dependent etching rates
- Example: a (111) plane will etch much slower than a (100) plane in an alkaline etching bath

Micro and Nanofabrication (MNF)

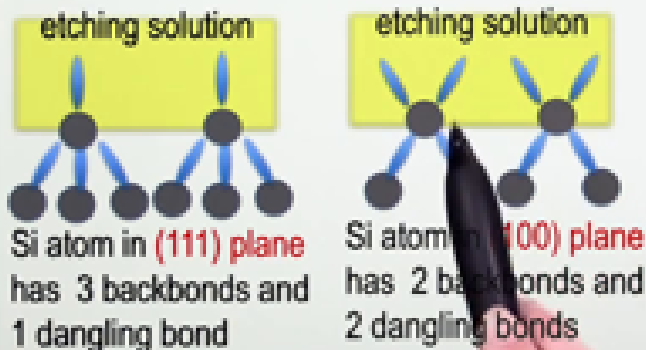
and one dangling bond which is interfacing with the etching solution. So this bond can be attacked by chemical molecules from the etching solution.

notes

summary

7m 43s





- A Si atom located in a certain plane is differently 'anchored' to the back of the substrate and has a different number of dangling bonds that are in contact with the etching solution
- This can give rise to plane-dependent etching rates
- Example: a (111) plane will etch much slower than a (100) plane in an alkaline etching bath

Micro and Nanofabrication (MIM)

A silicon atom within a (100) plane has only two backbonds

notes

summary

7m 54s



Etch mechanism for an atom in the (100) plane

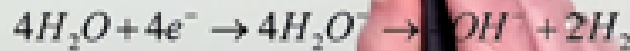


Si atom in (100) plane has 2 backbonds and 2 dangling bonds

- Four hydroxyl groups bind to a Si atom and the molecule $\text{Si}(\text{OH})_4$ moves into the solution



- In the solution $\text{Si}(\text{OH})_4 \rightarrow \text{SiO}_2 (\text{OH})_2^{2-} + 2\text{H}^+$
- Four electrons are injected into the valence band of Si and stay at the surface
- These electrons 'reduce' H_2O and form OH^- ions and H_2



Micro and Nanofabrication (MIM)

and two dangling bonds pointing in the etching solution. The second type of silicon atom is hence less well anchored to the silicon wafer and will be more easily etched away. An example of such an etching bath is potassium hydroxide or KOH solution. In such a bath, 4 hydroxyl ions bind progressively to a silicon atom in a two-step process leading to the formation of this molecule. This molecule is called *silicic acid*. It is converted in the solution to this molecule and into two protons. The four electrons that came from the four hydroxyl ions

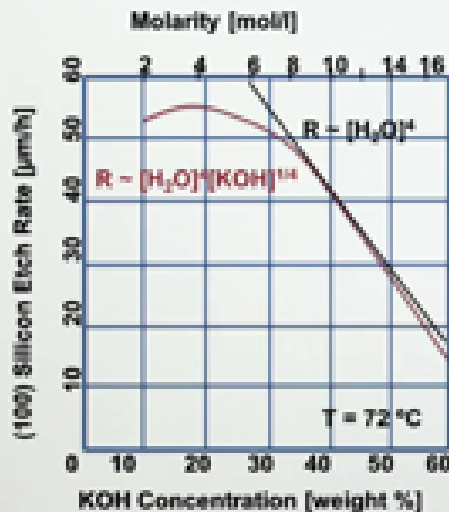
notes

summary

8m 3s



KOH etch mechanism for an atom in the (100) plane **EPFL**



(after Seidel et al., J. Electrochem. Soc. 137, 3612 (1990))

- The OH^- ions generated at the Si surface react in the oxidation step, while the OH^- concentration in the bulk solution does not play a major role

- Reaction rate

$$R = k[H_2O]^4[KOH]^{1/4}$$

- Four water molecules are needed in the reaction explaining the power 4 for $[H_2O]$
- OH^- ions are generated by water explaining the small power $1/4$ for $[KOH]$
- Etch rate in anisotropic etching is reaction rate-controlled and thus temperature-dependent

Micro and Nanofabrication (MNM)

have been injected in the silicon. These four electrons, they are used here to generate four new hydroxyl ions so that there is no charging of the silicon and the etching continues.

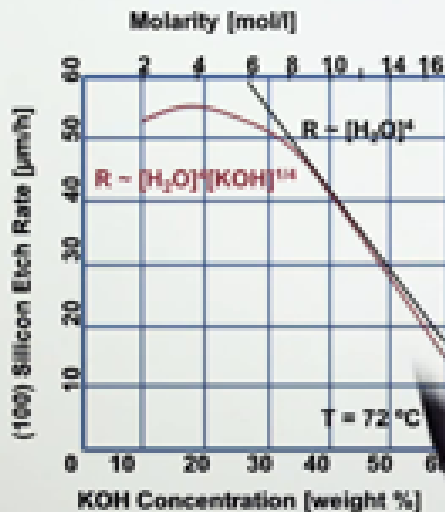
notes

summary

9m 1s



KOH etch mechanism for an atom in the (100) plane **EPFL**



(after Seidel et al., J. Electrochem. Soc. 137, 3612 (1990))

- The OH^- ions generated at the Si surface react in the oxidation step, while the OH^- concentration in the bulk solution does not play a major role

- Reaction rate

$$R = k[\text{H}_2\text{O}]^4 [\text{KOH}]^{1/4}$$

- Four water molecules are needed in the reaction explaining the power 4 for $[\text{H}_2\text{O}]$

- OH^- ions are generated by water explaining the small power $1/4$ for $[\text{KOH}]$

- Etch rate in anisotropic etching is reaction rate-controlled and thus temperature-dependent

Micro and Nanofabrication (MIM)

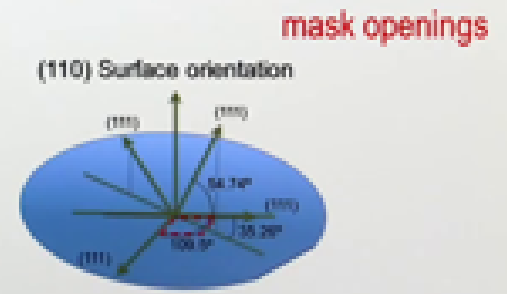
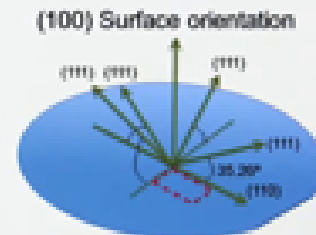
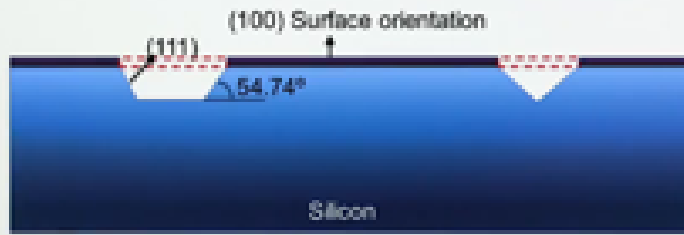
The four hydroxyl ions that are generated at the silicon surface originate from water molecules and not from hydroxyl ions initially present in the KOH solution. The reaction rate of the KOH etching bath can be written as this formula and between brackets, you have the molar concentrations. So this is the molar concentration of water, if there is more water, the concentration of water is higher. The power of four gives the water concentration the most prominent importance, while the KOH has only a power of $1/4$. The red curve shows the actual etching rate as a function of the KOH concentration. And we indeed see if there is more KOH dissolved in the water, the etching rate goes down. The black curve gives the power of four dependence on the water molar concentration.

notes

summary

9m 24s





Micro and Nanofabrication (MNF)

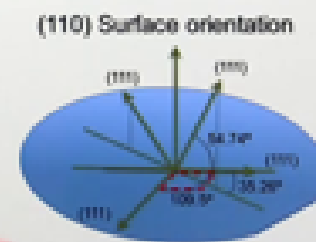
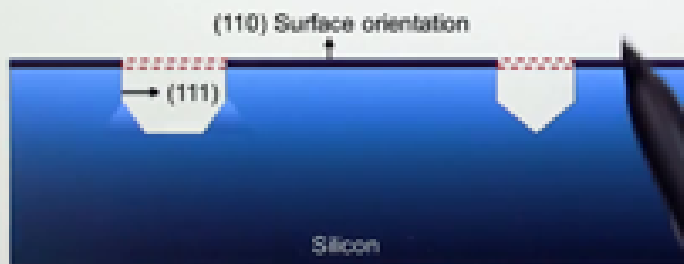
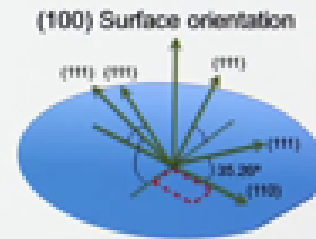
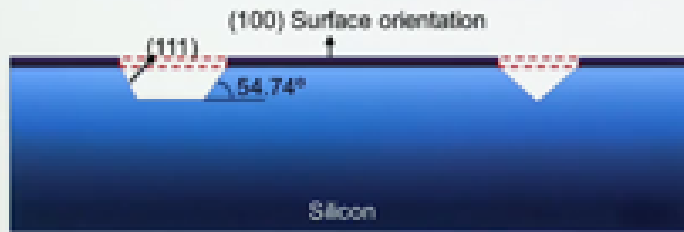
Note that this etching rate was for atoms on a (100) plane while to first order, there is no or very, very little etching of atoms on a (111) plane.

notes

summary

10m 36s





mask openings

Micro and Nanofabrication (MNF)

We draw here again our wafer with (100) surface orientation and cover it completely with the masking layer, except for a rectangular opening that is oriented along the (110) direction.

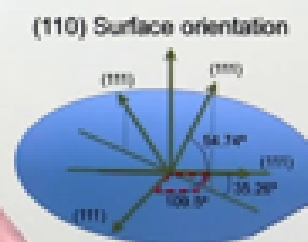
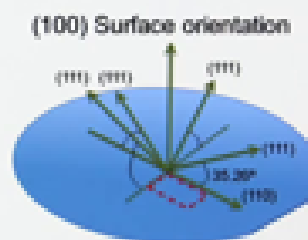
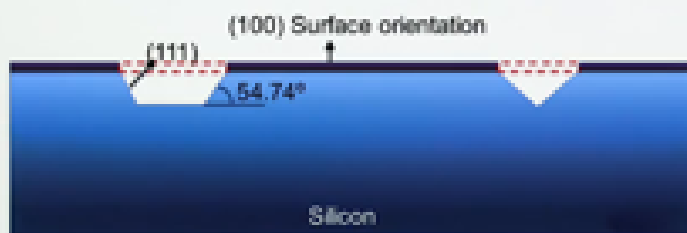
notes

summary

10m 52s



Anisotropic etching profiles



mask openings

Micro and Nanofabrication (MNF)

The diagram on the left side shows the same wafer in cross section

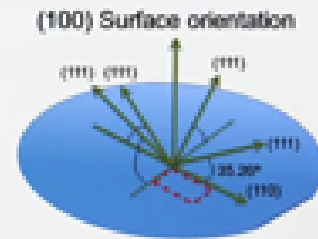
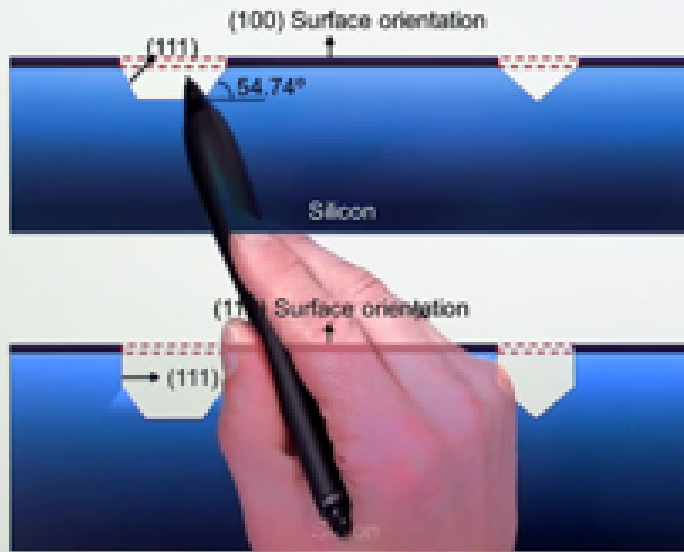
notes

summary

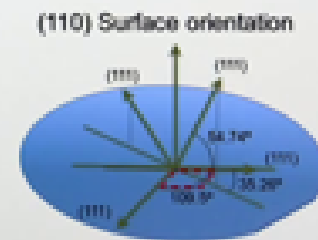
11m 13s



Anisotropic etching profiles



mask openings



Micro and Nanofabrication (MNF)

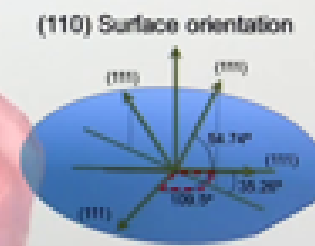
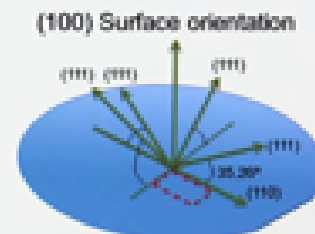
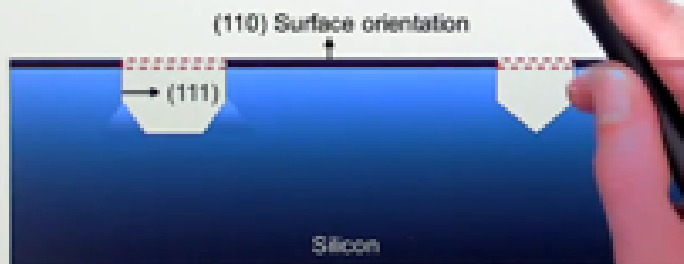
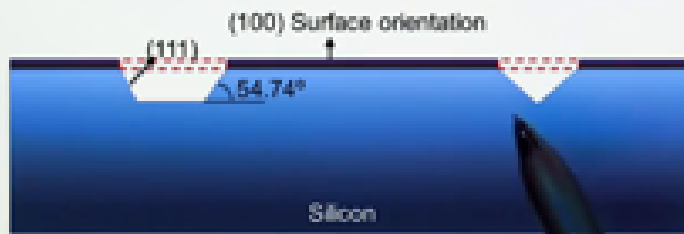
with two of these rectangular openings also indicated by the dashed lines. Atoms along the (100) plane will be etched away.

notes

summary

11m 14s





mask openings

Micro and Nanofabrication (MIM)

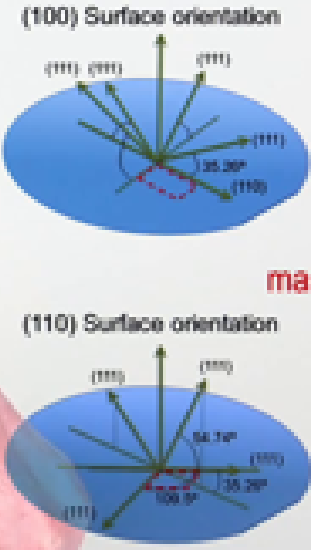
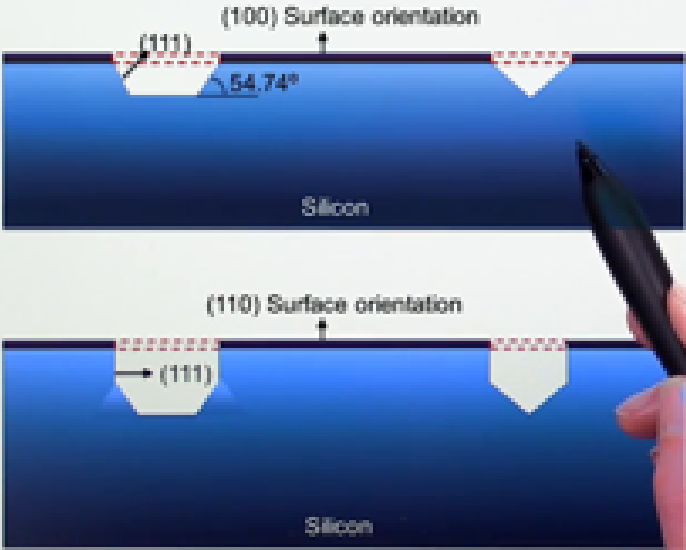
So etching will go vertical and if one encounters a (111) plane like here or here, there will be no etching. So gradually, the (111) planes will become visible.

notes

summary

11m 29s





Micro and Nanofabrication (MNF)

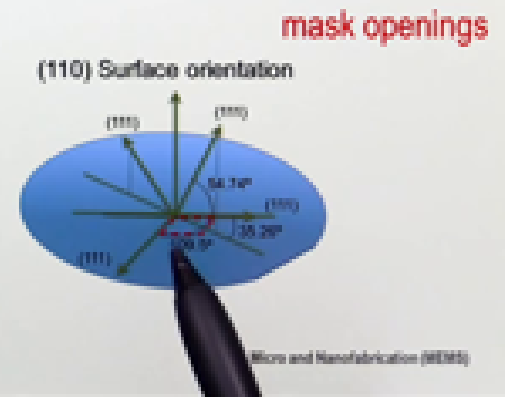
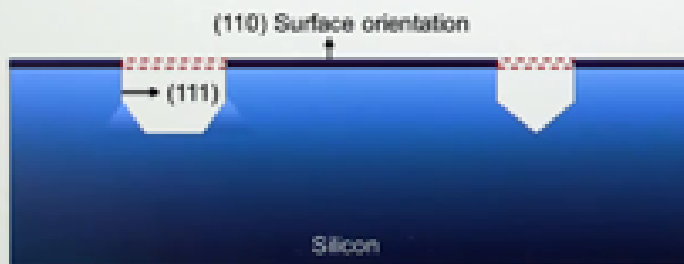
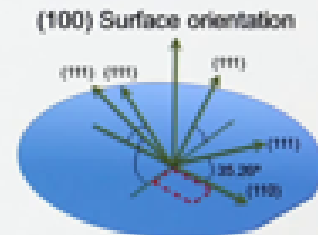
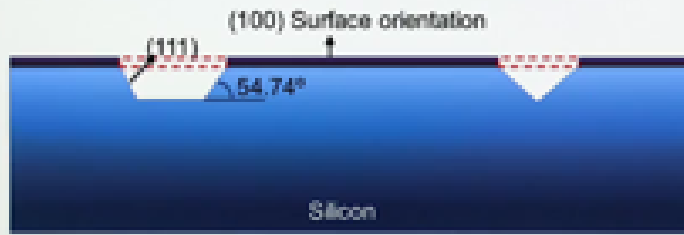
The hole here has reached the final V shape

notes

summary

11m 47s





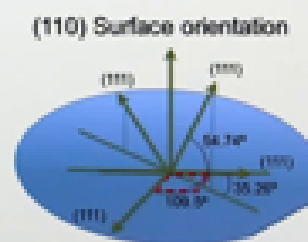
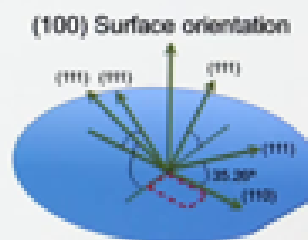
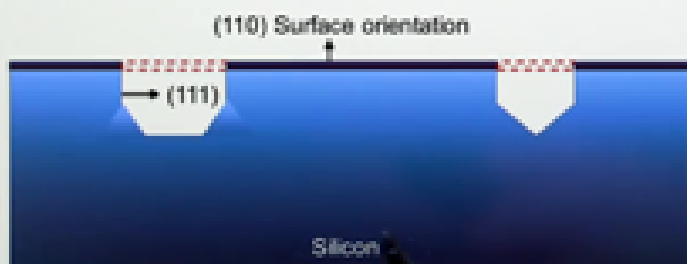
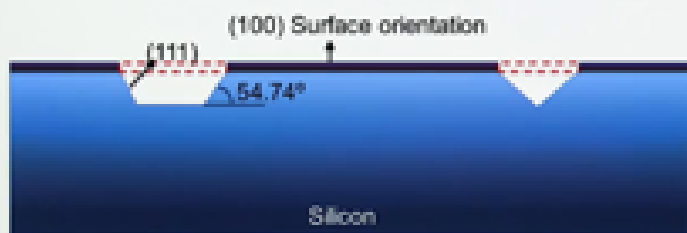
and no further etching will happen. In a similar way, we can draw again our wafer with (110) surface orientation, cover it completely with a mask material and make now an opening in the mask, given by this dashed line again.

notes

summary

11m 50s





mask openings

Micro and Nanofabrication (MNF)

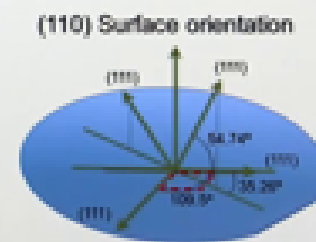
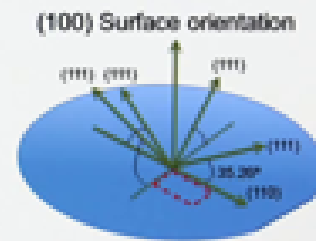
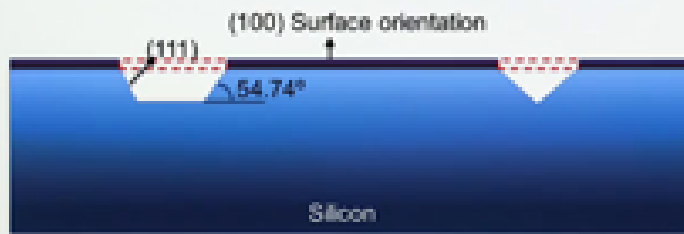
So this opening is parallel to the (111) directions.

notes

summary

12m 13s





mask openings

Micro and Nanofabrication (MNF)

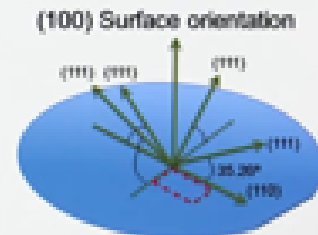
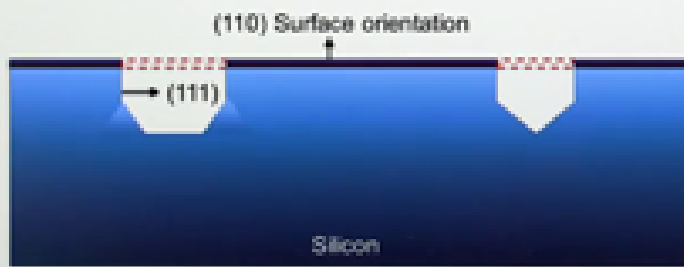
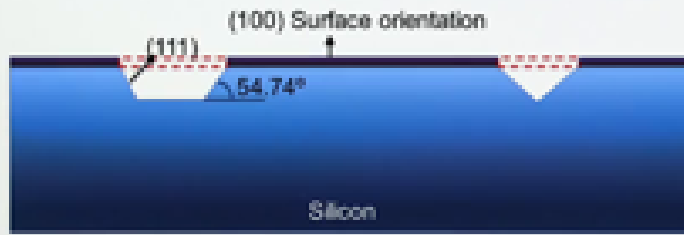
If we look to the cross section of the wafer after etching, we see following profiles with the structure on the right

notes

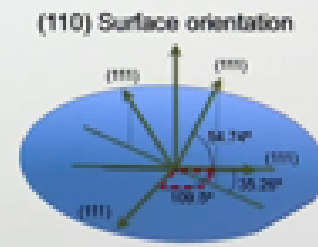
summary

12m 21s





mask openings



Micro and Nanofabrication (MIM)

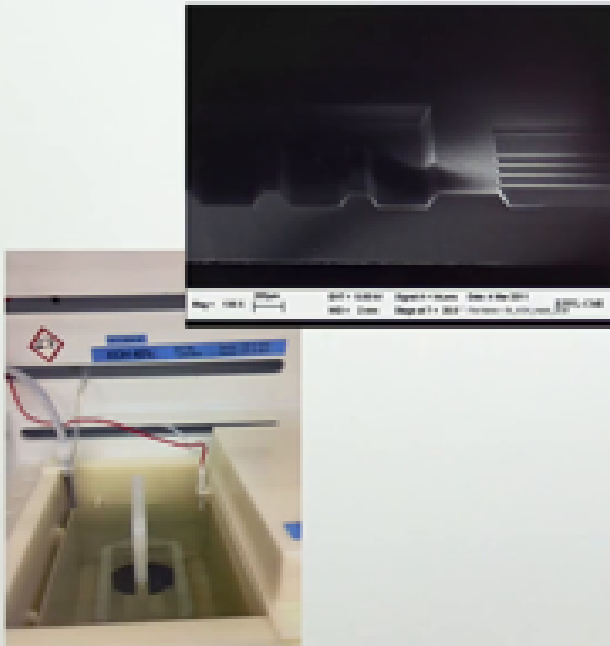
representing a hole in its final state where only (111) planes are in contact with the KOH solution, and this (111) plane indeed is vertical.

notes

summary

12m 29s





- Anisotropic etching possible in alkaline aqueous solutions like KOH, NaOH, LiOH, CsOH, NH₄OH
- Aqueous KOH is most 'popular' etchant, a typical bath is composed of 20 wt% KOH, 16 wt% propanol and 64 wt% water. The bath is operated under agitation at 80 °C
- The etching anisotropy ratio for different Si planes is (111):(110):(100) \approx 1:600:400
- The bath is relatively safe and non-toxic

Micro and Nanofabrication (EPFL)

Anisotropic etching is possible in different alkaline aqueous solutions but the most popular solution is the KOH bath. It is typically composed of 20 weight percent of KOH, 16 weight percent of propanol and 64 weight percent of water. The bath is typically operated under agitation at 80 degrees Celsius. These are the etching anisotropies for different silicon planes. Here we see that the (100) plane etches 400 times faster than the (111) plane. So the (111) plane etching rate is not completely zero.

notes

summary

12m 43s





The etching rate of a (110) plane is 600 times higher than that of a (111) plane. The picture shows the result after a KOH etching process and one recognizes typically these V-shaped channels and holes. And this is the KOH etching bath.

notes

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summary

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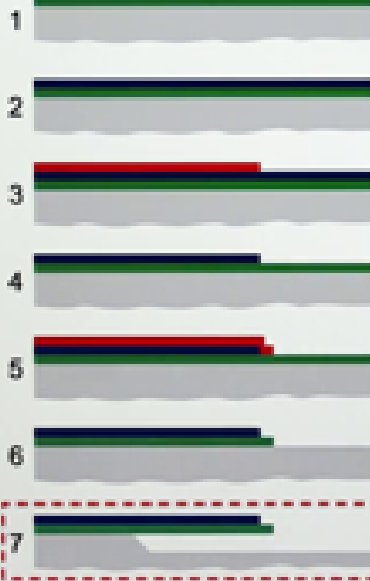
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.....

13m 37s

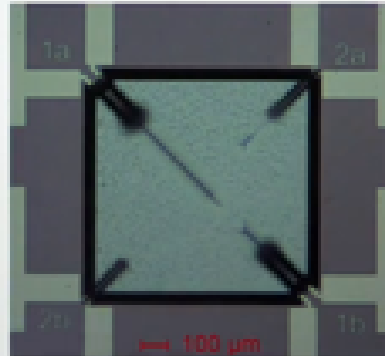


Si SiO₂ Cr PR



Step 7: Si etch

- Anisotropic Si etching in KOH
- Beams are released and bend upward because of residual stresses in SiO₂ and Cr thin films



Optical microscope



SEM

Micro and Nanofabrication (MNF)

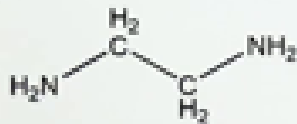
KOH etching was used also in the final step of our case study of the thermo-mechanical actuator. It was the process step that released the cantilever beam from the wafer by anisotropic underetching of the silicon. While there are several options that can be used to underetch,

notes

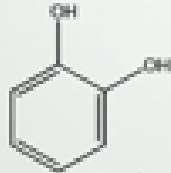
summary

14m 34s





ethylenediamine



pyrocatechol



pyrazine

- Alkaline organics also result in anisotropic etching.
Examples: ethylenediamine pyrocatechol (water) (EDP) and tetra-methyl ammonium hydroxide (TMAH)
- A typical EDP bath is composed of 75 wt% ED, 13.5 wt% of the chelating compound pyrocatechol, 0.5 wt% of the 'smoother' pyrazine and 11 wt% water. The bath is operated at 70-100 °C
- Ionization of ED produces OH^- ions
$$\text{NH}_2(\text{CH}_2)_2\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_2(\text{CH}_2)_2\text{NH}_3^+ + \text{OH}^-$$
- The etching anisotropy ratio for different Si planes (111):(110):(100) \approx 8:50:200

Micro and Nanofabrication (MNF)

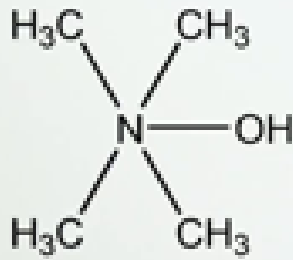
such as dry plasma etching, and isotropic silicon etching, anisotropic etching of silicon was used here due to its simplicity and efficiency for this type of structure. The inclined side walls of the etched hole immediately make it clear that we used an anisotropic etching process. Also so-called *alkaline organic baths* are used for anisotropic silicon etching. A well known example is the ethylenediamine bath with addition of pyrocatechol molecules, so-called *EDP* bath. It is composed typically of 75 percent of ethylenediamine,

notes

summary

15m 2s





Tetramethylammonium hydroxide

- A typical TMAH bath is composed of 38 wt% TMAH (25% solution in water), 4 wt% of Si powder and 58 wt% water. The bath is operated at 90 °C
- The Si serves for seasoning the bath and provides protective compounds for Al contacts during etching, for example
- The bath can be used in transistor fabrication, as it does not contain alkali metals like Na and K
- The etching anisotropy ratio for different Si planes is $(111):(100) \approx 1:10$

Micro and Nanofabrication (MNF)

13.58 percent of pyrocatechol, a half percent of pyrazine, and 11 percent of water. Ionization of the ethylenediamine produces this ion and the hydroxyl ion. That is why it becomes an alkaline bath. Pyrocatechol is a chelating molecule. Two of such molecules with these fingers can grab a silicon atom and transport it into solution. We also present here, the etching anisotropy rates for different silicon planes using this bath. So the ratio of the etching rate for example, of a (111) plane and a (100) plane is 8:200.

notes

summary

15m 49s





- Real and reciprocal space
- Anisotropic etching mechanism
 - Different bond strength for a Si atom in a different plane
 - (111) plane etches very slow
- Different alkaline etching baths
 - KOH
 - EDP
 - TMAH

Micro and Nanofabrication (MIM1)

A third popular bath is the tetramethylammonium hydroxide bath or TMAH bath which produces good results by adding a few weight percent of silicon powder in the bath during etching. This is a so-called seasoning of the bath and it results in better aluminium contacts that are preserved during the etching. The etching anisotropy is lower than for the two other baths. In this lesson, we have discussed the anisotropic etching of silicon. We gave a reminder of real and reciprocal space vectors whereby a reciprocal space vector is characterizing a crystal plane. We explained the anisotropic etching mechanism which is due to a difference in bond strength for a silicon atom on a different plane. We found that a (111) plane etches very slowly. Finally, we discussed different alkaline etching baths like KOH, EDP and TMAH.

notes

summary

16m 48s

