

Course material

Course:

Micro and Nanofabrication (MEMS)

Video:

6.3 Wet etching 3

Concepts (extracted from automatically generated subtitles):

Isotropic etching of silicon. Chemical etching bath. Hole injection. Positive voltage. Bath consisting of nitric acid. Electrochemical etching of silicon. Iso-etch curve. Highest etching rates. Low temperature. Double positive charge. Etching rate. N-doping. Acetic acid. Hf bath. Creation of porous silicon.



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



[to video](#)

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...

notes

summary

0m 0s





- Hydrofluoric acid + nitric acid + acetic acid bath ('HNA' bath)
 $HF + HNO_3 + CH_3COOH$ (A)
for Si etching
- HF bath for electrochemical etching and for creating porous Si

Micro and Nanofabrication (MNF)

Now we will discuss a chemical etching bath

notes

summary

0m 1s



- Overall reaction



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for the isotropic etching of silicon, which is a so-called *HNA* bath consisting of nitric acid, HF, and acetic acid. Then we present the HF bath for electrochemical etching of silicon, and for creation of porous silicon.

notes

summary

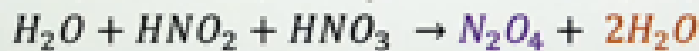
0m 5s



- Overall reaction



- In acidic media, the Si etching process first involves **hole injection into the Si valence band** by an oxidant. In the absence of photons or applied field, holes are produced by HNO_3 in an autocatalytic process



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The HNA bath has three components, two of which are active in the etching, namely, the nitric acid and the HF. The acetic acid is a diluent for reducing and for better controlling the etching rate. That is why we only see these two components in the reaction. The silicon is etched from the substrate, and transported into the solution in the form of this molecule, which is called *fluorosilicic acid*, while the HNO_3 and HF are consumed. Now we will detail what happens during etching. In acidic media, like nitric acid, the silicon etching process first involves hole injection into the silicon valence band by the oxidant, in this case, the HNO_3 , which is meaning the same as removing an electron out of the valence band of silicon. In the absence of light, or an electric field, holes are produced by nitric acid in an autocatalytic process. HNO_3 , when it is dissolved in water, partially splits up in HNO_2 , and it is this HNO_2 that reacts with HNO_3 to form this compound, N_2O_4 , or dinitrogen tetroxide, and water. The dinitrogen tetroxide decomposes in 2NO_2 , or nitrogen dioxide molecules,

notes

summary

0m 28s



- Si^{2+} combines with OH^-

$$Si^{2+} + 2OH^- \rightarrow Si(OH)_2$$
- Generation of SiO_2 with release of H_2O
 Overall oxidation reaction



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while the water splits up in two hydroxyl ions and two protons. The nitrogen dioxide is the active molecule that generates the holes, denoted as h^+ , as well as NO_2^- , or so-called *nitrite ions*. The nitrite ions recombine with protons to form HNO_2 molecules, while the holes charge the silicon. We see here that a nitrous acid, the HNO_2 , is regenerated because, in the beginning, we spoke of an autocatalytic process. HNO_2 is not consumed, but the HNO_3 , in a way, is consumed, as, on the other side, we have $2HNO_2$ molecules. Now we have

notes

summary

2m 25s



- Si^{2+} combines with OH^-
 $Si^{2+} + 2OH^- \rightarrow Si(OH)_2$
- Generation of SiO_2 with release of H_2O
Overall oxidation reaction



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a double positive charge on the silicon, and this combines with two hydroxyl ions

notes

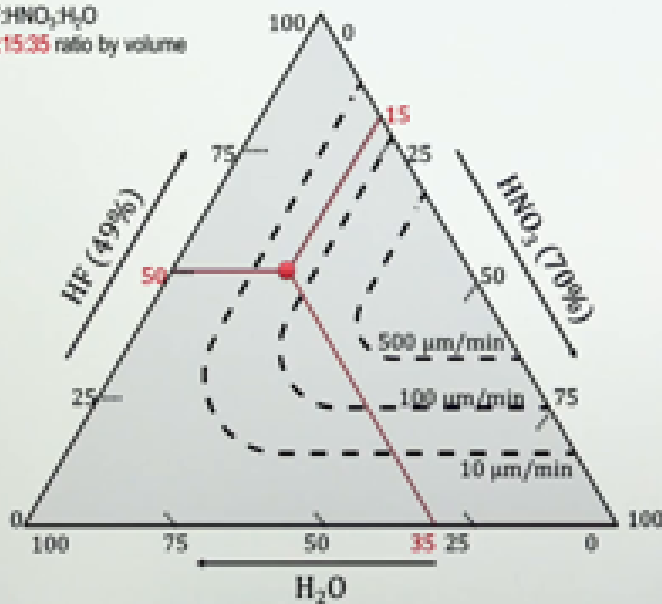
summary

3m 30s



Ternary diagram for HNA bath

HF:HNO₃:H₂O
50:15:35 ratio by volume



- The concentration of the three basic components HF, HNO₃, and H₂O, are plotted along one of the axes
- A point in the triangle corresponds to a unique composition of the bath
- One can attribute to each point a physical property of the bath with that respective composition, e.g. the etching rate
- Iso-etch curves can be plotted

Micro and Nanofabrication (MNF055)

to form this $\text{Si}(\text{OH})_2$ group, and these groups on the surface, they recombine to generate silicon dioxide and the release of water. The overall reaction until now is the transformation of silicon in silicon dioxide, under the reduction of nitric acid into nitrous acid. Now the HF comes into play. We have seen, in the previous lesson, how HF reacts with the silicon dioxide, forming the molecule, fluorosilicic acid, and water. As said before, the acetic acid is not entering in these chemical reactions because it's a diluent. Also, water can be used in the bath as a diluent, by the way. A ternary diagram like this allows to plot the three chemical components of the bath on a two-dimensional sheet of paper.

notes

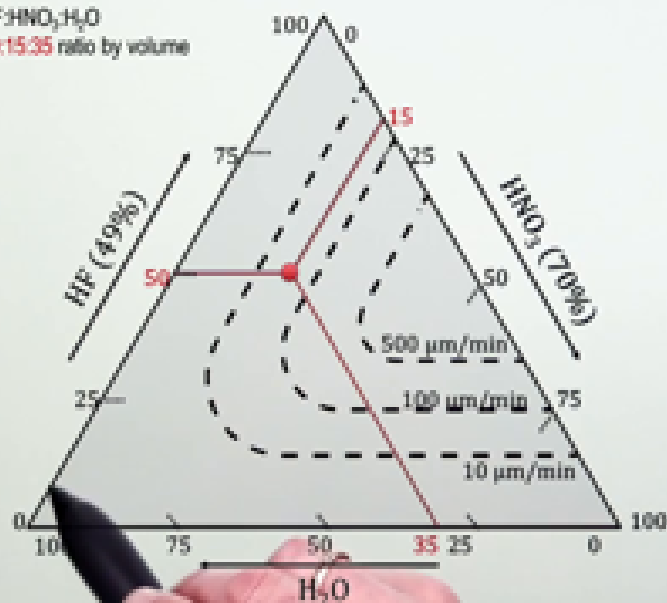
summary

3m 38s



Ternary diagram for HNA bath

HF:HNO₃:H₂O
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Micro and Nanofabrication (MNF)

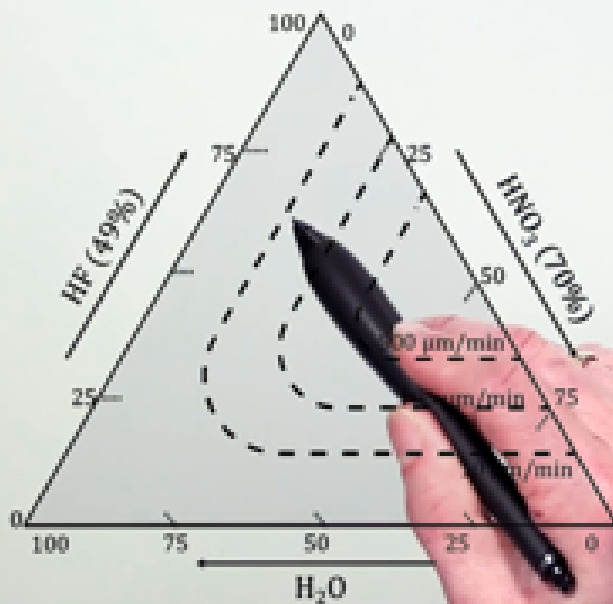
So, this is an axis where we plot

notes

summary

4m 49s





- For high HF concentration, the iso-etch curves are parallel to the lines of constant HNO_3 and HNO_3 controls the etching rate (oxidation process is limiting)
- For high HNO_3 concentration, the iso-etch curves are parallel to the lines of constant HF and HF controls the etching rate (removal of the oxide is limiting)
- Maximum etch rate when HNO_3 and HF are equilibrated and when H_2O concentration is low

Micro and Nanofabrication (MNF055)

the HF concentration from 0 to 100%. This is an axis where we plot the nitric acid concentration from 0 to 100%, and on this axis, we plot the diluent, in this case water, from 0 to 100%. Each point of the triangle corresponds to a unique composition of the bath. For example, this red point corresponds to a mixture with 50% pure HF, 15% of HNO_3 , and 35% of water, and you see, together, this forms 100. This red line says that, all along this line, if I continue just like that, there is, everywhere, 50% of HF, and, when moving on the line, one interchanges HNO_3 with water. So, the more we go in this direction, more will there be HNO_3 and less water. Now we can measure the etching rate for each bath composition, and then plot the ensemble of points where the etching rate is the same. This is a so-called *iso-etch curve*. For example, this dashed line corresponds to all compositions of the bath, where the etch rate is 500 micrometers per minute. On this line, it is 100 micrometers per minute. We see that the highest etching rates are obtained in a zone of the diagram where one has about the same quantities of HNO_3 and HF, because both are needed, and where there's only a small concentration of water, which is logical. For high HF concentration, that's in this region, the iso-etch curves are parallel to the lines of constant HNO_3 , and this means that it's the HNO_3 concentration that controls the etching rate.

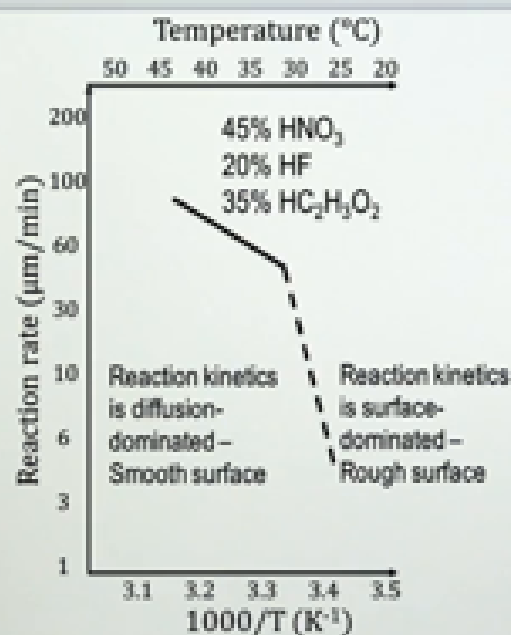
notes

summary

4m 53s



Arrhenius plot of the etching rate



- At low T, the etching reaction is limiting the process and the activation energy is associated with the oxidation reaction
- At high T, diffusion of active species in the bath is limiting and etching leads to smooth surfaces
- Etching rate depends on agitation of the bath at high T



(after Schwartz and Robbins, J. Electrochem. Soc. 108, 365 (1961))

Micro and Nanofabrication (MNF02)

In fact, there is enough HF, and the little number of HNO_3 molecules limit the etching rate. And, in the same way, for high HNO_3 concentration, the iso-etch curves are parallel to the lines of constant HF concentration, and this means that HF controls the etching rate, as there are relatively few HF molecules, and the removal of the oxide represents the limiting step.

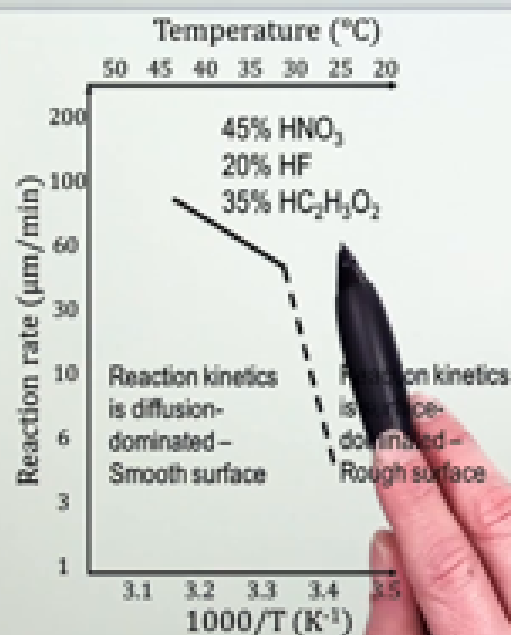
notes

summary

7m 13s



Arrhenius plot of the etching rate



- At low T, the etching reaction is limiting the process and the activation energy is associated with the oxidation reaction
- At high T, diffusion of active species in the bath is limiting and etching leads to smooth surfaces
- Etching rate depends on agitation of the bath at high T



(after Schwartz and Robbins, J. Electrochem. Soc. 108, 365 (1961))

Micro and Nanofabrication (MNF05)

Here, we present the temperature dependence of the etching rate for a bath of particular composition, namely that having 45% of nitric acid, 20% of HF, and 35% of acetic acid.

notes

summary

7m 50s



- Etch rates for
 - Si : 50 $\mu\text{m}/\text{min}$ (66% HNO_3 , 34% HF)
 - SiO_2 : 30-80 nm/min
- SiO_2 can be used as mask material
- For very deep etching, Au or Si_3N_4 masks are required
- Photoresists do not withstand strong oxidising agents like HNO_3
- Problems with isotropic etchants
 - Etch rate is agitation-dependent
 - Isotropic etching = charge transfer process, hence there is etch rate dependence on dopant type and concentration. N- or p-type regions with dopant concentration of 10^{17} cm^{-3} or smaller etch 150 times slower than for high dopant concentrations → technique is used for wafer defect analysis

Micro and Nanofabrication (MNF055)

The x-axis is linear in one over the temperature, while, on the top, we have plotted the temperature corresponding to this linear axis. At low temperature, that means at a high one over T value, the etching reaction is limiting the process, and the activation energy, that is the slope of this curve, is associated with the oxidation reaction which is the slowest. After etching, the surface shows some roughness. At high temperature, that means at low one over T, diffusion of the active species in the bath is limiting the etching reaction, and the etching results in smooth surfaces. At high temperature, this etching rate depends now on the agitation of the bath, as, by agitation, transport of molecules is better than by diffusion only. Also, when diffusion is limiting the reaction, when one has a wider opening in the mask, this results in deeper etching, as the access for the reactive molecules is facilitated. What are the mask materials that one can use in an HNA etching process?

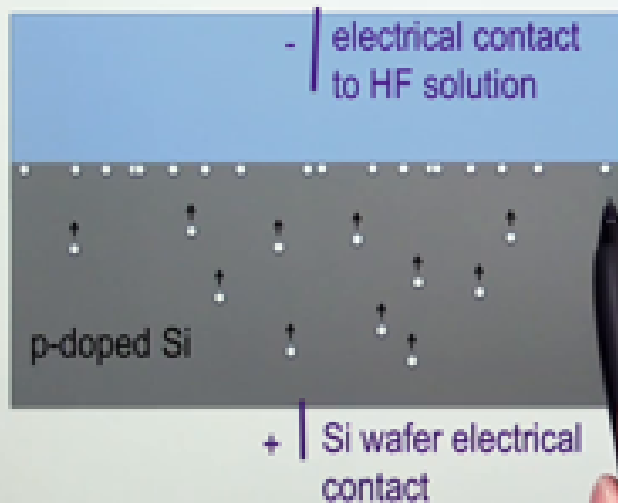
notes

summary

8m 5s



Isotropic etching of p-doped Si with electrical bias EPFL



- A high temperature aggressive chemical etching process can be replaced by an electrochemical procedure utilising a milder solution, thus allowing a simple photoresist mask to be employed
- Oxidation can be promoted by a **positive voltage bias applied to the p-Si** causing an accumulation of holes h^+ in the Si at the Si/electrolyte surface
- No need for HNO_3 , 5% HF solution can be used for etching

Micro and Nanofabrication (MNF)

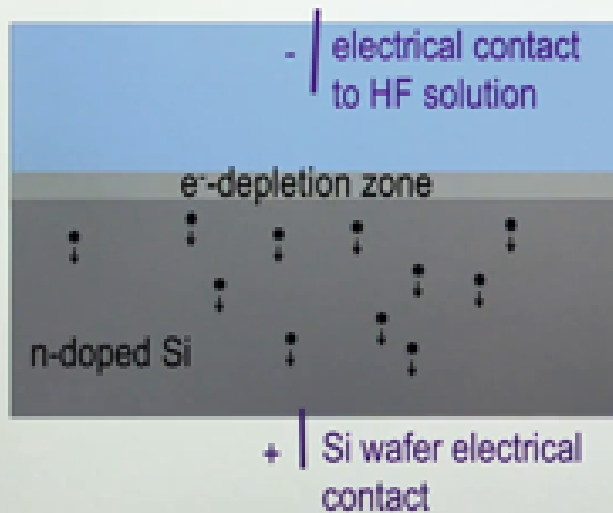
If one is at a temperature where the silicon etching rate is 50 micrometers per minute, the silicon dioxide etching time is in between 30 and 80 nanometers per minute, much slower, so that silicon dioxide can be used as a mask when etching silicon. For very deep etching, one needs gold or silicon nitride masks. One cannot use photoresists as they do not withstand long to a strong oxidizing agent like nitric acid. There are some issues with isotropic etchants, like the etch rate that is agitation dependent and depends on the local condition of the bath. We explained, during the discussion of the isotropic etching mechanism, that there is a hole transfer process to the silicon, hence, there is an etch rate dependence on the dopant type and concentration of the dopant in the silicon, so it makes a difference whether one has n- or p-type regions doped in the silicon, or if they have different dopant concentrations. However, this characteristic can be used to reveal the number of defects on the surface of a silicon wafer, for example. One etches the surface, and defects can be etched faster, and can then be directly seen on the surface. We explained that etching of silicon in an acidic solution involves the transfer of a hole from the nitric acid to the silicon. It is possible to replace this chemical injection of a hole by an electrochemical procedure, utilizing a milder solution, so that a photoresist mask can be used. Suppose one has a p-doped silicon wafer, and that one attaches a conducting wire where one puts a positive voltage bias. By this, holes will be transported in the silicon, and accumulate at the silicon electrolyte interface.

notes

summary

9m 37s





- Applying a **positive voltage bias to an n-Si wafer** causes a depletion of electrons e^- in the Si at the Si/electrolyte interface
- No etching occurs, except when the voltage is so high that electrical breakdown occurs, transporting h^+ to the interface

Micro and Nanofabrication (MNF)

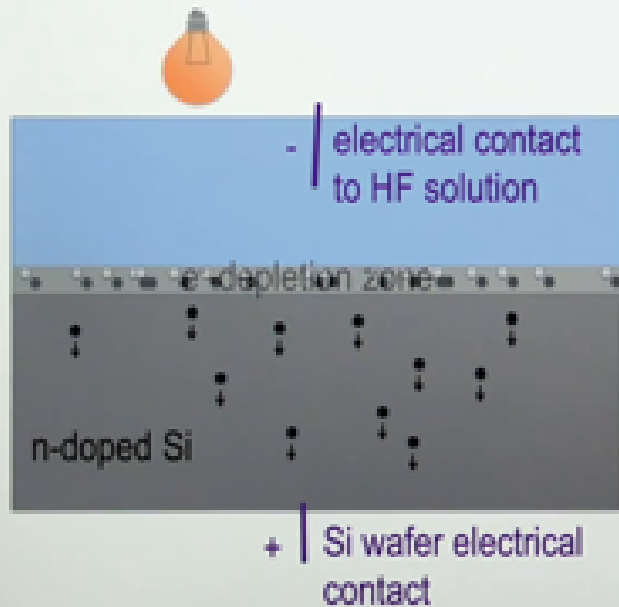
We have seen that these holes are essential for oxidation, so the oxide forms, and this can now be removed by just having an HF solution, so there is no longer nitric acid, but there will be etching because there was oxidation at the surface.

notes

summary

12m 1s





- Applying a **positive voltage bias** to the **n-Si** causes a depletion of electrons in the Si at the Si/electrolyte surface
- Applying light generates e^- and h^+ pairs in the depletion region that electrical
- Electrons are transported to the positive voltage
- Holes h^+ at the surface promote oxidation
- Etching occurs

Micro and Nanofabrication (MNF)

Now we change to silicon with n-doping, and we attach, again, a wire to the back of the substrate, and apply the positive voltage. What will happen now is that the electrons, that are the mobile carriers, will be attracted towards the positive voltage and we will get, here, an electron depletion zone at the contact with the solution. No etching will occur in a diluted HF solution as no holes are present at the surface, except if this positive voltage would be so high that there is an electrical breakdown by which holes can be transported to the surface.

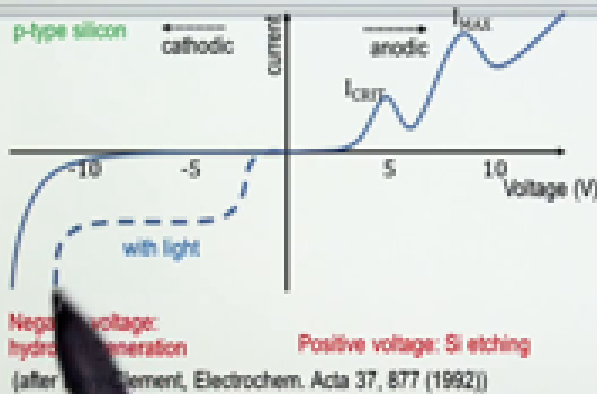
notes

summary

12m 26s



Current-voltage characteristics



- At i_{MAX} and higher, **bright electro-polishing** occurs. HF is depleted at the surface and a high concentration of holes builds up at the interface
- Positive voltage: Si etching
- Negative voltage: hydrogen generation
- At i_{CRIT} , there is partial dissolution of Si. This leads to formation of **rough and porous Si**. Condition: low current densities, i.e. limiting the oxidation of Si due to hole deficiency

Micro and Nanofabrication (MNF005)

We are now again in the case with n-type doping, and we have applied here a moderate positive voltage. If we now add to the setup a light source, we create photons that generate electron hole pairs, and the electrons go towards the positive voltage, while the holes remain here. Now there can be oxidation, and, subsequently, the HF etches away the oxide. We are now looking at the current voltage characteristics of p-doped silicon, which is put into the dilute HF solution. When we apply a positive voltage, we transport holes to the interface, due to which there is oxidation, and etching occurs. More voltage means more holes, means more etching, and it follows this particular behavior. If we apply a negative voltage, this attracts the holes to the wire, leaving a depletion of holes at the interface. No reaction is occurring, hence, no current is flowing, except if the voltage is so high

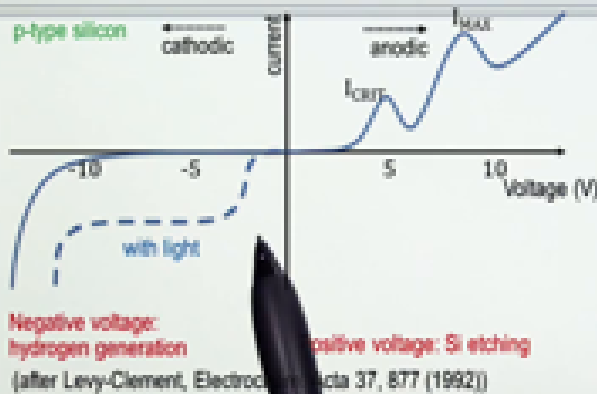
notes

summary

13m 17s



Current-voltage characteristics



- At i_{MAX} and higher, **bright electro-polishing** occurs. HF is depleted at the surface and a high concentration of holes builds up at the interface
- Positive voltage: Si etching
- Negative voltage: hydrogen generation
- At i_{CRIT} , there is partial dissolution of Si. This leads to formation of **rough and porous Si**. Condition: low current densities, i.e. limiting the oxidation of Si due to hole deficiency

Micro and Nanofabrication (MNF055)

that one has electrical breakdown. If one now shines light, the photons generate electron hole pairs, the electrons of which stay at the interface,

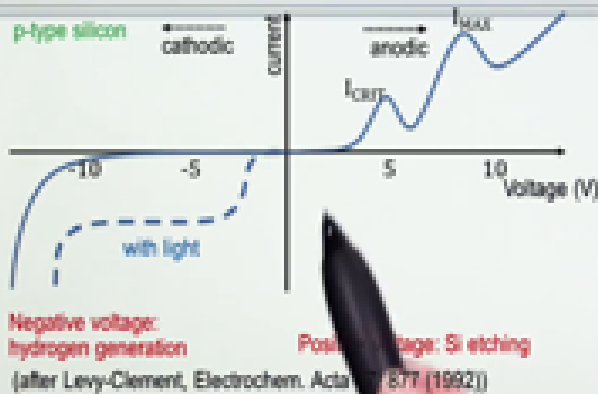
notes

summary

14m 44s



Current-voltage characteristics



- At i_{MAX} and higher, **bright electro-polishing** occurs. HF is depleted at the surface and a high concentration of holes builds up at the interface
- Positive voltage: Si etching
- Negative voltage: hydrogen generation
- At i_{CRIT} , there is partial dissolution of Si. This leads to formation of **rough and porous Si**. Condition: low current densities, i.e. limiting the oxidation of Si due to hole deficiency

Micro and Nanofabrication (MNF005)

and these electrons recombine with protons from the electrolyte, thereby generating hydrogen gas. So, under negative voltage bias, there is a current that is generated by the generation of hydrogen and not by etching.

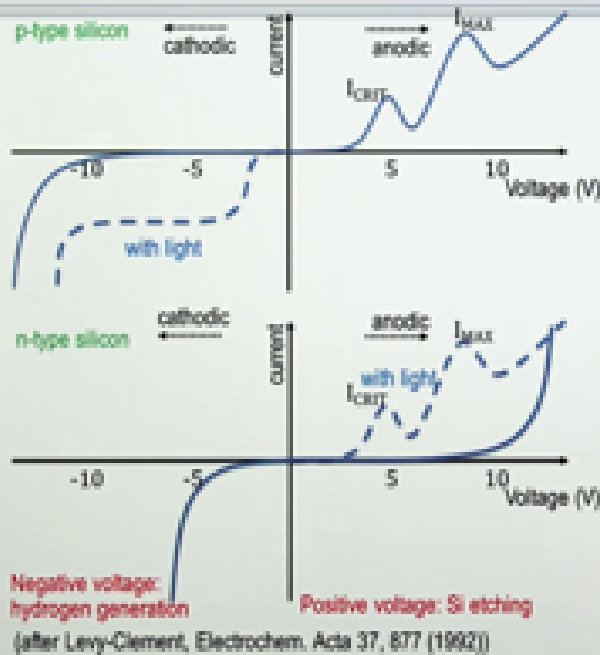
notes

summary

14m 55s



Current-voltage characteristics



- At i_{MAX} and higher, **bright electro-polishing** occurs. HF is depleted at the surface and a high concentration of holes builds up at the interface
- Positive voltage: Si etching
- Negative voltage: hydrogen generation
- At i_{CRIT} , there is partial dissolution of Si. This leads to formation of **rough and porous Si**. Condition: low current densities and light intensity, i.e. limiting the oxidation of Si due to hole deficiency

Micro and Nanofabrication (MNF055)

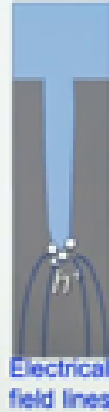
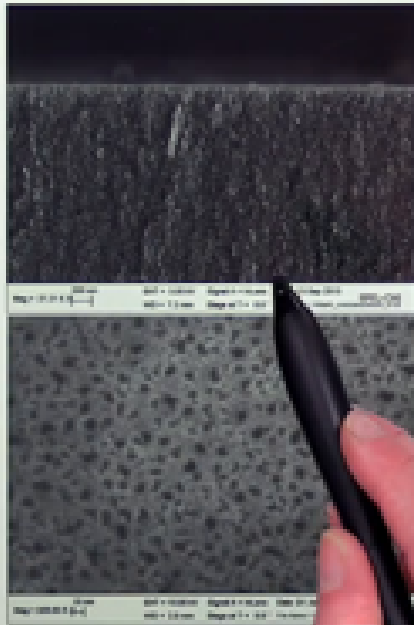
If you look back again at the positive part of the curve, we know that, for high currents, the surface that was etched appeared bright. Due to the high number of holes, electro-polishing results. If one is at lower current, the number of oxidation events is reduced and one gets only locally oxidation and etching, resulting in a rougher surface. If we now take an n-type doped silicon wafer, and bring it in the diluted HF solution, and we apply a negative voltage, electrons will be transported to the silicon electrolyte interface, in a straightforward way, to generate hydrogen gas. If we apply a positive voltage we will have the depletion layer effect, which we have introduced before, so there will be no current except if there is voltage breakdown. Shining a light to the wafer creates holes at the interface leading to oxidation and this positive current, represented by the dashed line. A condition for realization of porous silicon is to have a low current and low light intensity in order not to have too many holes

notes

summary

15m 20s





- Pore sizes in diameter from 2 nm to 10 μm are possible
- Very high-aspect ratio (250) pores maintained over several mm distance
- For currents below i_{MAX} , a dense network of fine holes forms: microporous Si (pore size 2-20 nm)
- Macropores (size up to 10 μm) have been reported for n-type Si under high anodic voltage (>10 V) and low current density
- Macropore formation is a self-adjusting mechanism with holes h^* kept on a pore tip by the electrical field

Micro and Nanofabrication (MNF055)

at the electrolyte silicon interface. The top picture shows

notes

summary

16m 49s





- Chemistry of isotropic wet etching in a HNA bath
- Electrochemical etching in a HF bath
- Realisation of porous Si by electrochemical etching in a HF bath

Micro and Nanofabrication (MN101)

a cross-section of an n-type wafer, the surface of which was transformed into porous silicon. The lower picture shows a view from the top of the wafer. Pores can be created with diameters ranging from a few nanometers to 10 micrometers. The bigger pores are obtained by applying a high positive voltage, resulting in electrical breakdown of the n-doped silicon. The smallest pores are realized at low voltages and by tuning the intensity of the light source. Pores can be very narrow and very deep, with an aspect ratio of up to 250: they can be 250 times deeper than wide. These very long and narrow pores originate from the fact that the electrical field lines are focused towards the bottom of a pore, where the holes accumulate, resulting in oxidation only there, and continuing etching in the vertical direction. If one has too many holes, the holes will be everywhere, and one will not have porous silicon. If there are just enough holes, only etching will occur at the bottom of the hole, and the pore becomes deeper and deeper. This ends our lesson on the isotropic wet etching of silicon. We have first explained the chemistry involved in isotropic wet etching in a so-called HNA bath, pointing out the importance of having holes originating from the nitric acid at the silicon surface to induce oxidation, after which the HF removes the oxide. Then we have explained the electrochemical etching in an HF bath. If you apply a positive voltage to the wafer, holes can be transported to the surface, and the nitric acid can be avoided. We then explained how porous n-type silicon can be made by electrochemical etching in an HF bath by applying moderate current and light intensities so that the number of holes at the surface is limited, and they accumulate only at the bottom of the pores.

notes

summary

16m 54s

