

A Brief Introduction to Micro Sensors
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Lecture-14
TMAH etching

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Tetra –Methyl Ammonium Hydroxide (TMAH)

Advantages of TMAH

- Low toxic
- Highly selective to oxide and nitride compared to KOH
- High Si etch rate
- Compatible with CMOS processing



Credit: Prof. K. N. Bhut, IISc Bangalore



We are discussing about anisotropic etching. And in the last class, we have discussed like how KOH can anisotropically etch silicon. Now today, we will talk about 1 new chemical that is tetra methyl ammonium hydroxide or TMAH. And TMAH also etches silicon anisotropically, means; in all in all the direction the etching rate is not same.

Now, as you understand by now that; the etching rate is depends on the silicon (Refer Time: 01:11) or which direction you are etching. So, changing the chemical that property does not change; that means, that the 1 0 0 will have like the medium kind of etching rate 1 0 0 1 1 0

will have highest etching rate and 1 1 1 will have the lowest etching rate. But, in those directions; etching like the magnitude of etching rate will change definitely with different kind of chemicals.

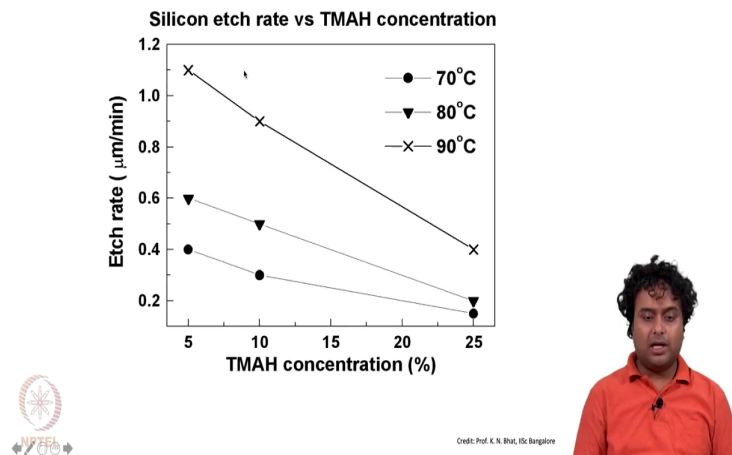
So, first of all, what are the advantages of using TMAH. The first point is that; this is very much less toxic like KOH is more toxic than TMAH. Then this is highly selective to oxide and nitride compared to KOH; that means, like if we compare that how much of oxide is etched in 1 minute in terms of KOH and TMAH then in TMAH the etching rate like the etch the oxide etching will be lesser.

So, these gives us high selectivity; that means, that as we know that, the these oxides. As you know that; these oxides are actually used as masking layer right. So, as we discussed earlier that; if we have 2 etch 10 micron of silicon and in that time, if we need to etch let us say for 30 minutes for that and by that time if SiO_2 is etched by let us say 100 nano meter then, we need atleast 100 nano meter SiO_2 . Otherwise, the masking layer will get etched off.

Whereas, for TMAH this etching rate is even smaller. So, we can use even lesser thickness of masking layer, if we use TMAH etching. In the silicon, for the silicon etching rate is pretty high, like comparable to KOH or even higher and then the fourth point is the most important that is the compatible with CMOS processing; that means, like whatever micro electron is sensors we use today.

All are based on CMOS circuitry then, for that all the processes are not actually compatible of CMOS processes with the CMOS devices, but TMAH does not do any kind of harm to the CMOS device or it cannot it does not change the mobility of the semiconductor.

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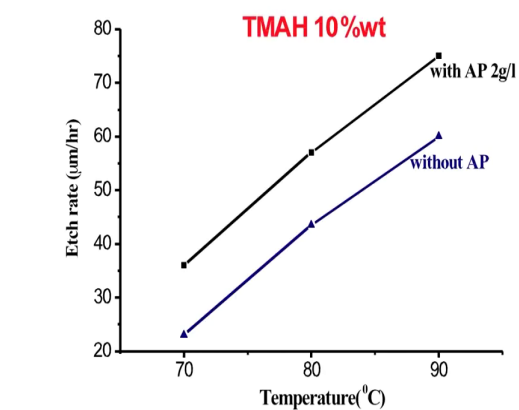


So, it is compatible with CMOS processing. Now, where we are comparing silicon etch rate with TMAH concentration right. So, as you are seeing that; as we increase the TMAH concentration then, the silicon etch rate decreases. And it goes from like this graphs are drawn at different different temperature. So, at 70 degree centigrade the etch rate is the lowest compared to the other two temperature.

So, the another point what you can note from this graph that is; we are increasing the temperature, the etch rate is getting higher and higher. Whereas, as we are increasing the concentration etch rate is getting smaller and smaller and it almost from 1.1, it goes down to; goes down to about 0.4. So, it almost decreases by about 50 percent or more than that while we are increasing the TMAH concentration from 5 percent to 25 percent.

So, these temperature and the concentration both are like control parameter for TMAH etching. We can select suitable temperature and concentration and accordingly can select the etch rate or can choose the etch rate.

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Addition of Ammonium Persulphate(AP) gives smooth surface and increases etch rate

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Credit: Prof. K. N. Bhut, IISc Bangalore



Ammonium phosphate, adding ammonium phosphate gives us another control on TMAH etching. If we add 10 percent of ammonium phosphate in TMAH etching in the TMAH solution then, we can see that the etch rate actually increases right. So, without ammonium phosphate; the etch rate is lesser as you can see from this graph for all the temperatures that are 70, 80, and 90. For all the temperatures, the etch rate is lesser for the TMAH etching with the ammonium without the ammonium phosphate whereas, as we increase as we added ammonium phosphate then we are getting higher etch rate.

And also it gives smooth surface. Which is also a requirement for many of the device application, because on top of that we deposit new material like metal electrode or some other kind of contact and it will be the contact will be better, if we have a smooth surface. So, adding ammonium phosphate also gives us a advantage from that perspective.

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TMAH etching of Silicon

- Anisotropy (111) : (100) ~ 1:10 to 1:35
- Selectivity against Oxide > 1000
- Si : $1 \times 10^{21} / \text{cm}^3$ Boron doped Si ~ 100 : 1
- Aluminium Passivation can be achieved if the etchant is contains Silicic acid



So, now these are the important points related to TMAH etching. First of all is anisotropy. And here you can see that the 111 plain to 100 plain can have a selectivity of 1 is to 10 to 1 is to 35; that means, that the by the time 1 nanometer of 111 plain will be etched it 100 plain will be etched by 10 nanometer to 35 nanometer. And that depends like whether it will be 10 nanometer or 35 nanometer that depends on the TMAH concentration temperature etcetera parameters, but anisotropy will be always there.

So, the etching rate for 111 will be lesser much lesser than the 100 plain. Next important point is selectivity ok. And as you can see here that the selectivity to against oxide is more than 1000. So, this is very important because by the time we need to we etch 1 micron of silicon only 1 nanometer of silicon dioxide will be etched with TMAH.

So, this can protect the silicon layer that whichever reason, we need to protect we can use silicon dioxide layer to protect that because, this was the very good selectivity against oxide. Then similar to KOH also; if we dope the silicon with boron then also we have a very high selectivity like 100 is to 1. So, boron doped silicon is a silicon will be etched to 100 nanometer, boron doped silicon will be etched to only 1 nanometer. So, this is another way of getting different kind of patterns by doping different regions according to our required design.

Final thing is aluminium passivation. So, in some cases we need were that after etching that etched region will be passivated or protected. If we add some amount of silicic acid to the TMAH then, we can get aluminium passivation in the region were it is etched.

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Comparison of Etchants

KOH :
Simple etchant
Use it when no electronics is involved
Thicker mask layer
Good Anisotropy

EDP (Ethylene Diamine Pyrocatechol):
Use when P⁺ etchstop is present
Highly toxic

TMAH :
Highly compatible with CMOS



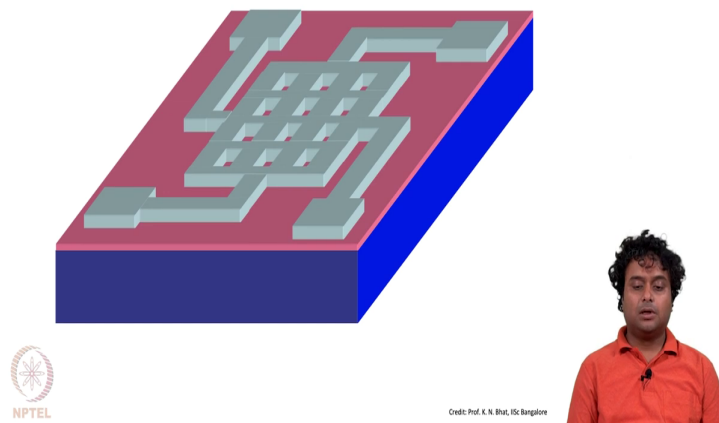
Now, if we compare KOH EDP and TMAH then we can see that KOH simple etchant simple etchant and you can use it when no electronics is involved. Because, there are possibility of k plus ion actually, penetrating into silicon and changing the conductivity of the silicon semiconductor. So, let us say we are making some kind of electronic devices and there we need for a particular transistor; we need specific mobility of the transistor of the semiconductor.

So, in that case if we use KOH etching then there is a possibility that KOH like the k plus ion might change the conductivity or the semiconductor layer or the silicon layer. So, in those cases you should not use KOH and we need a thicker mask layer because as we were saying that KOH etch is SiO₂ also very (Refer Time: 09:21) not as aggressive as silicon, but compare to TMAH it has much higher etching rate.

So, we needed thicker masking layer. And for KOH also we get very good anisotropy. The next etchant EDP; which we have not discussed in this course we should use were have P plus etchstop because P EDP has a very good selectivity with respect to p plus etchstop, but the negative point is this is highly toxic whereas, TMAH is not toxic and this is highly compatible with CMOS and it has all the good points of KOH also and you can use it while making the CMOS technologies also.

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KOH Etching Convex corners

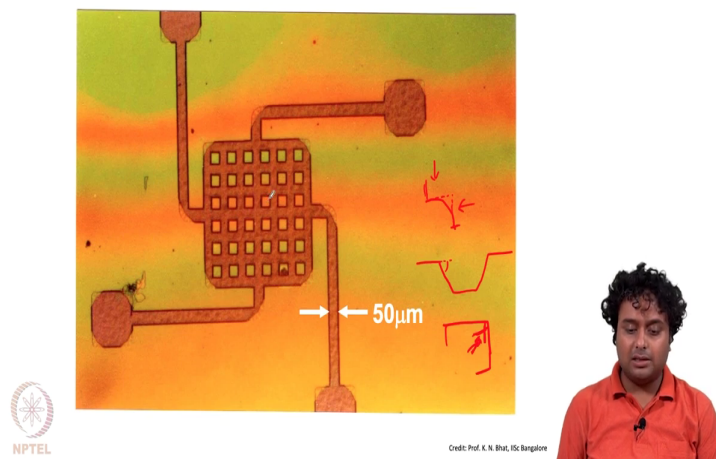


Now, another aspect of KOH etching is convex corner. So, that we will explain now with the help of these design. So, let us say this is the design we need to etched and this top white portion whatever you can see here; these are the, this is the design right and this is the masking layer and ultimately we are etching this pink layer which is which let us say is silicon. Now, as you can see there this regions are protected.

So, these regions will not get etched which is just below the white layer; this will not get etched and all the open areas will get etched very easily. So, ultimately you should see the same kind of pattern in the silicon on this pink layer. This white region can be some kind of polymer which is used as a masking layer or SiO_2 .

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Micrograph of patterned sample after etching



So, rounding up of these convex corners should not be there according to the design, but what happens is; see this like this corner actually attacked from both directions like this direction as well as this direction. As we have seen for KOH etching that we get a profile like this right. Where this angle is 54 degree 54.7 degree and then this plane is 111 plane, plane is 111 plane.

Now, both of these like this face is also and this face and this face also both of these faces will have 111 plane, but this 111 plane will get easily attacked from this direction as well as this 111 plane or the slope will get easily attacked from this direction. So, because of that this

convex this corner will get etched even more easily. So, this convex corner will get etched even more easily. And so, we will get something like this where the actual surfaces something like this right it get etched.

In case of concave corner the 111 plains actually the protective plains actually join or merge here. So, there is no point were the material can actually attack from this direction because, in this direction actually this 111 plain is there. So, the concave corner are not etched aggressively where to compared to the convex corners.

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Prevention of the etching of Convex Corners

Method -1: Add 30% tertiary - butanol solution or Isopropyl alcohol to the 30% KOH solution

Method -2 : Modify the etch- mask as shown in the next example

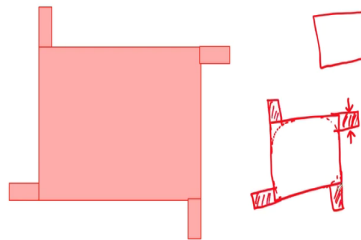


Now, there are different ways to prevent this convex corner etching. The first method is that; we can add 30 percent tertiary butanol. The first method is we can add 30 percent tertiary butanol solution or IPA to the 30 percent KOH solution ok. So, these will reduce the etching

rate at the convex corner and another way is that etch will modify the mask according to our design. So, that we will discuss in the next slide like this.

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Etch-Mask with corner etch compensation



The width of the corner beam must be about twice the thickness of the square pattern

Programs that simulate the structure to achieve by etching with a given mask are commercially available



So, technically we need a mask like this. Now, as you have seen the convex corner, because of the convex corner etching it will become like this right. Now, what we can do is; we can modify our design to add this extra portions here. Now, adding this extra portion what we have done that; now there does not exist any convex corner.

There does not exist any convex corner only here is some concave corner which will not be effected because of that and this extra region is also such that it will go under etching and it will it can get removed by the time the complete etching is done. So, this dimension also we need to keep in mind. So, that by the time the our desired depth is etched this region also should get etched.

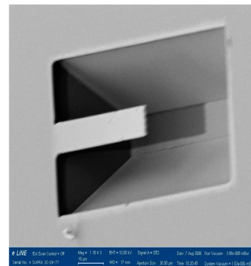
So, ultimately the design after etching should come like this without any convex corner and this regions will also not be there because of the under etching. And for that purpose; the width of the corner beam must be about twice the thickness of the square pattern. And there are actually, commercially available programs are there which can; if we input our design then accordingly it creates or modifies the mask.

So, that the convex corner etching will not be there. Why it should be actually twice? Because, let us say the thickness of the thickness of this layer which we actually want to etch is about 1 micron right. So, by the time we etch it will go in the vertical direction by 1 micron. Now, in this 1 micron, it will try to etch laterally also right. From this direction as well as from this direction it will etch 1 micron.

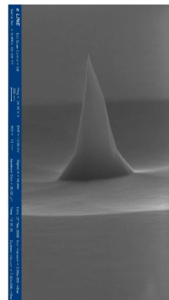
So, if it is both side if it is coming 1 micron then if the width is about 2 micron, then only by the time it etches 1 micron vertically it will etch 2 micron horizontally. So, this complete region will get etched off. And the convex corner also will not be there it will be sharp corner.

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Cantilever Beams and AFM tips by Anisotropic WCE



SiO₂ Cantilever
L= 65 μm, W= 15 μm, thickness = 0.52 μm, Stiffness k=0.134N/m



AFM tip defined by <411> planes

Credit: Prof. K. N. Bhut, CMSE, IISc Bangalore



Finally, I am going to show this two patterns which are made by using anisotropic weight etching. And there, you see this cantilever and this is the sem image or scanning electron microscope image of a real silicon silicon dioxide cantilever which was made by KOH etching. Because, silicon got etched, but SiO₂ did not get etched. So, accordingly SiO₂ remain as a free standing beam and this is the hollow region you can see; you can see the shadow of the cantilever at the bottom part of the change.

And this cantilever is about length is about 65 micron with this 15 micron and thickness is about 500 nanometer. So, this is this was done by KOH etching. And the next example is of a of an AFM tip. And AFM tip is etched by just like that; this is let us say the mask and below there is silicon. Now all the sides silicon will get etched and 111 planes will get opened up.

Now, as this 1 because of the convex etching as this 111 planes are getting etched from the convex corner also. So, the 411 plane comes into the picture like 411 411 planes get opened up and because of that see that this region, if this is the mask then the middle portion will get etched at last. Because, it will take time for the etchant to come in contact with this right and the side regions will get etched fast.

So, it will ultimately become like a pyramid shape, because the top region will get first etched. So, the etching rate for the most region will get etched from the top initially and then as it is opens up slowly it goes down and then it etches from the bottom also and by the time it reaches our desired depth the top portion it has almost reached the central point.

So, you get a sharp tip which is used for atomic force microscopy. So, this two both the both of this structures were made in (Refer Time: 18:33) by (Refer Time: 18:35). And with this we will stop for this class and next time we will discuss on lithography.

Thank you.