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Lecture – 43 Wet etching Basics

In this lecture, we shall look at specific recipes of wet etching under the subtractive manufacturing module.

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Wet Etching N	Nechanism	CENSE
	Fresh Etchant	
	Stagnant layer ① ③	
	Etching mask	
	Film	
1. Reactant trar – Remember boun	isport to surface across a 'stagnant' layer dary layer of CVD?	
2. "Selective" & -Causes etching	controlled chemical reaction	
3. Transport of –Must be soluble	by-products away from surface in the solvent	
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In a prototypical wet etching reaction, we have a film, an etching mask (a photoresist or a hard-mask), and an etchant. There are three steps in etching. This fresh etchant must reach the film you want to etch by passing through a 'stagnant' layer. Once it reaches the surface, it must react and form byproducts. Those byproducts must again go through this stationary layer back to the bulk of the solution, and this process must continuously happen to get a consistent etch rate.

Why is there a 'stagnant' layer? It is the layer adjacent to the etch-surface, where the byproducts generated at the surface accumulate, and you have a low concentration of the fresh etchant. If you remember the CVD lecture, you would see the parallels. In the absence of active flow, the way the material transports is through diffusion. The fresh etchant must make its way through this layer to get to the etch-surface, and the byproducts, when they leave. You can break this layer a bit by agitation or stirring. That

increases the etching rate a bit. But even in those cases, there is always a microscopic layer of junk.

Once it reaches the surface, you need to think about the etching chemistry. The byproducts must be soluble. If you are etching silver and form insoluble silver chloride, that is not a good etching recipe. The soluble byproducts need to diffuse back into the solution. The other concern is selectivity. Generally, you etch the film using an etching mask. The recipe should have some selectivity against the masking layer; otherwise, it restricts the etch-depth.

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As we had in CVD, the etch rate can have two limiting steps; surface reaction and diffusion (of the etchant or the byproduct). In the surface reaction rate limited regime, the slowest step is the surface reaction. Since both the diffusion flux and the reaction flux must be equal in equilibrium, the surface reaction rate decides the etch-rate, not the diffusion. If the surface reaction rate is very high, you wait on fresh etchant to get to the surface, and in that case, you are in the diffusion rate limited regime.

As discussed during CVD, surface reactions or chemical reactions are often very strongly dependent on temperature. If the etching rate is surface reaction rate limited, you can expect the surface temperature to play an outsized role. The etching rate can go up to 2x for just $10 - 15^{\circ}$ C heating of the solution. The advantage is you can etch at a higher rate. The disadvantage is that you have to worry about selectivity, degradation of the resist,

and non-uniformity. It is one thing to say that I will heat the solution by 10°C, and quite another to uniformly heat it by 10°C everywhere. Merely putting it on a hot plate does not always achieve that.

If you are diffusion rate-limited, stirring and agitation can increase the etch rate because these make the etchant diffusion faster. The disadvantage is that non-uniformity might crop up; it is tough to get uniform etching across the wafer with stirring and agitation, especially if it is large. Imagine you have a 12" wafer, and you are trying to agitate the etchant by swirling the beaker. It is challenging to get the beaker's swirl exactly right everywhere on the wafer. The liquid's movement might be lower in the middle and higher at the edge. That might cause non-uniformities.

The surface reaction rate limited regime is more probable under low temperatures, dilute, or weak etchants. At lower temperatures, the reaction rate falls and becomes a slow step. If the etchant is dilute, diffusion will be fast. Weak etchants, by definition, do not react with the surface very fast. So, in these cases, the etch rate is reaction rate limited. You get a diffusion rate limited regime at high temperature, concentrated, or aggressive etchants. The diffusion becomes fast at high temperatures, but the reaction rate becomes faster, making diffusion the slow step. Diffusion through a film doesn't scale as quickly with temperature as the surface reaction rate. For concentrated etchants, the diffusion is slower. Aggressive etchants, by definition, have a fast chemical reaction rate on the surface. Hence, these are diffusion rate limited.

The surface finish in these two cases is often slightly different. The surface reaction rate is often anisotropic. The chemical reaction can have different rates on various facets of a crystal; (110) might be slightly different from (111) because of the structure and surface energy. These factors change the etching rate, leading to possible anisotropy and also roughness. If you start with a smooth film, but if the different facets of the film etch at different rates, by the end, you might see micro roughening. Diffusion does not depend on direction. It does not show any dependence on facets, and the reaction tends to be isotropic. It leads to smooth, shiny surfaces because there is no difference at the micro and macro scales. If that is the goal, you should use a diffusion-limited recipe. For anisotropic etches, you can move towards surface reaction rate limited regimes.

Typically, the contamination in a surface reaction rate limited regime is low. That is because this often happens for dilute etchants. The byproducts or junk left-over on the surface are less. Diffusion rate-limited recipes often are viscous, concentrated, and leave a residue. So, the contamination can be high, especially if out-diffusion is a problem. It can also happen if the byproducts are not very soluble.

Typically, the application for surface reaction rate limited regime is cleaning. In a very general sense, cleaning is usually is mild etching. We are trying to remove the contamination on the surface, but it is an etching recipe. Diffusion rate-limited etching is often actual etching. If you want to make a $10 - 20 \mu m$ deep hole in silicon, you probably will not have a dilute solution, but a concentrated, aggressive one, which is diffusion-limited.

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We are talking about wet etching, so I am using words like solvent and etchant. It creates the impression that we are only talking about chemistry. The fact is we are talking about electrochemistry. Most of the etching is an electrochemical process. The electricity does not come here explicitly; it is not like supplying current or applying voltage. The electrochemistry comes in because the etching process creates domains of positive and negative charges as it progresses. These domains form (and change) because of random perturbations. What is positive right now may become negative down the line. These domains alternatively act as anodes and cathodes and do the etching reaction that leads to material removal. Only when you appreciate that this is an electrochemical process where positive and negative charges play the role can you understand some of the second-order effects. For example, several etchants show a dependence on doping.

That is very hard to explain if it is entirely a chemical process because doping is less than ppm or ppb. Why should an impurity at parts per million or billion concentration change the bulk etch rate? If you look at this as an electrochemical process, it is easier to explain the doping dependent etch rate as doping changes the material's work function. Often defects in the semiconductor affect the etching rate. Again, this is very hard to understand if it is dislocation, which does not change the material's bulk properties too much unless you look at this as an electrochemical process. A defect can change the work function, bond energies, and hence, etching rates.

The etchant impurities also affect the etch rate as they may act like surfactants and enhance it or be retardant and reduce it. When we look at specific recipes, I will highlight what is happening at the anode or the cathode, but for this slide, the bottom line is, always think of wet etching as an electrochemical process.



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If you remember the CVD lecture, we discussed different types of chemistries you can use for deposition. The most common was reduction because most semiconductors tend to be reduced elemental semiconductors. It stands to reason that etching, which is a reverse process, will probably be oxidative. So, most etchants tend to be oxidative. The basic idea is the same as cleaning. Depending upon the metal or element, it should be soluble in an acidic or alkaline medium. If the oxide is insoluble, you hope to create a soluble complex that you can remove. The canonical or the general mechanism is something like this: start with a semiconductor M, oxidize it to MO_x , and dissolve that oxide either in an acidic or a basic solution or by creating a complex. Once it forms a soluble byproduct, the byproduct out-diffuses, exposing a new semiconductor that gets oxidized. We will keep using this concept again and again.

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HF: Isotropic SiO ₂ Etch	Censi
• HF Solutions are used to etch SiO ₂ –Mix 49% HF (conc.) with deionized water in various proportions –HF is consumed so [H ⁺] changes and hence etch rate changes $SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$	
 HF can be buffered with NH₄F to maintain [H⁺] at a constant level Mix 49% HF (conc.) with 40% NH₄F in various proportions Called buffered oxide etch (BOE) Etch rate is constant 	
$\rm NH_4F ightarrow \rm NH_3 + HF$	
 May contain surfactants –For improving wettability of silicon Masking layer: Si 	
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The most common etching is the isotropic etching of SiO2 using hydrogen fluoride (HF). You may find this familiar because we used dilute HF to remove the chemical oxide that forms during cleaning. The difference is now we are using it for etching thicker films of silicon dioxide. You can get HF in 49 % concentrated form from a vendor. You often dilute it with deionized water because the concentrated HF is a very reactive solution. For microfabrication applications, it etches way too fast and is difficult to control.

The primary mechanism by which HF etches SiO_2 is as follows. SiO_2 forms a soluble complex with HF - H_2SiF_6 . This soluble complex floats away, exposing fresh SiO_2 to HF's attack, and the mechanism continues. Notice that during this process, the HF gets consumed. The concentration of the H⁺ ion also changes. You can expect that the rate to change unless you put HF in significant excess, which is what we do in wet etching all the time. In microfabrication, we usually etch only a few nm or μ m. Even if you etch a full wafer, you are trying to remove somewhere between ng/min to μ g/min of material.

You do not need a large quantity of etchant at that lower material removal rate, probably only a few ml. However, you take a whole beaker and put the wafer. You always have a plethora or a significant excess of the etching solution. Even though you are consuming the etching solution, the absolute concentration doesn't change too much over the etching period. However, this assumption starts to break down if you have a very dilute etchant or don't have a lot of it. During cleaning, for example, we used 1:100 or 1:50 diluted HF. In those cases, you have to consider how much the concentration HF changes. To remove this effect from the picture and get much more reproducibility, you may use a buffer solution.

There are specific solutions that maintain pH. To keep an acidic solution's pH constant, put salt of a weak base and a strong acid. You form a buffer solution where the acidic pH stays at a certain level. We do something similar here. The goal is not to maintain the pH but to maintain the concentration of HF such that the reaction with silicon dioxide remains consistent. We add a little bit of NH₄F, a salt of a weak base - strong acid to the HF solution. If you put in the right amount for NH₄F, you can maintain an arbitrary concentration of HF, despite HF getting consumed because NH₄F starts to dissociate to make up for any loss in HF. Typically, we use the concentrated HF with ~ 40 % NH₄F in various proportions. This composition is called buffered oxide etch (BOE). You usually use dilute, not the concentrated solution.

For all BOE solutions, the etching rate tends to be uniform even if you do long etches. Why call it buffered oxide etch and not just by the chemical name? BOE also contains surfactants that help reduce the loading effect that we talked about while discussing uniformity. Sometimes, because of the surface tension, especially in wet etching, the etchant may not be able to penetrate a hole. Adding a little bit of surfactant solves that problem by reducing the surface energy. That allows the etchant to enter even small holes up to a level. The addition of the surfactants complicates the chemistry a little bit.

The chemists would often not give you the surfactant details because that is a trade secret; they give you only the etching rate. If you get an etching solution from a reliable vendor experienced in making etchant solutions for semiconductor fabrication, you just trust that everything is pure, and the chemistry will work. You need a masking layer for any etchant; For HF etching of SiO_2 , the masking layer is silicon itself. The great advantage of HF is that it etches SiO_2 well, but not silicon. During cleaning, we discussed some of the second-order effects. For example, if you expose silicon and HF for a long time, it will not etch it, but it might roughen it. That can still happen. However, by and large, silicon is an excellent masking layer for SiO_2 , or HF has a high selectivity against silicon.

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The etching rate of BOE or HF is the same. It changes with concentration, which is not hard to imagine. A concentrated solution of HF has more HF that attack SiO₂ better and, hence more etching. The good news is that this dependence is linear and thus very predictable. You commonly do SiO₂ etching at room temperature. Plot the rate versus the HF concentration. We touched upon this during the cleaning lecture; in semiconductor processing, we don't use standard concentration measures like molarity or normality, just proportions. For example, a 1:100 HF solution means one part of concentrated 49 %t HF and 100 parts of deionized (DI) water. The dilution 1:10 means one part 49 % concentrated HF and 10 part DI water. As you go from 1:100 to 1:10 on the log scale, the etching rate linearly increases. It varies over 100 times. Notice that the etching rate depends on temperature. At high temperatures, you get a higher etching rate. This plot is the etching rate for a commercial BOE from JT baker vs. temperature. Compared to 20° C, at 50° C, you get a much higher etching rate.

The etching rate can increase several times. It also highlights the fundamental concern: you must tightly control the surface temperature for uniform etching; minimal changes cause massive etching rate changes. These curves shift upwards if you increase the fluoride concentration. 1:5 will etch much faster than 1:50.

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The next canonical example we shall discuss is silicon nitride etch. BOE or HF can also etch silicon nitride, but the etching rate is much slower than silicon dioxide. For example, it is only 0.5 nm/min for a high-quality Si_3N_4 layer. We discussed the various methods of depositing SiO_2 and how they affected several properties like density, refractive index, etcetera, and etching rate. I had commented that the better the quality of a film, the slower the etching rate. For Si_3N_4 etching using HF, that rate is as small as 0.5 nm/min. Even for 10 nm, it takes 20 min; that is a long etch.

A photoresist is not a good masking layer because of the very long etch times. It does not hold up very well for that long. To prevent all of these issues, you often etch Si_3N_4 through a different acid, boiling H_3PO_4 . The challenge is photoresist does not withstand this. So, usually, the masking layer for this etch is SiO_2 , which is an example of using a hard mask. Whenever you do patterning using photoresist, you use a soft-mask because photoresist is a soft material. Here, you require a hard-mask; you first have to pattern the SiO_2 on top of the Si_3N_4 using HF and then use it as a mask to etch Si_3N_4 using boiling H_3PO_4 . The etching rate is ~ 10 nm/min for Si_3N_4 . H_3PO_4 doesn't etch SiO_2 or etches only 1-2 nm/min. That means you have a selectivity window of ~5. To remove 100 nm Si_3N_4 , you have to ensure that the masking SiO_2 is at least 20 nm. You may keep it at 40 nm or 50 nm to be a little safe.

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Etch Rate Dependence	ce			Cense
• Etch rates vary widely —Film quality —Deposition method —Temperature —Impurity in layers	with:			
	Etchant	PECVD SiO ₂ @ 450 C	Thermal SiO ₂ @1100 C	
	1:1 BHF	~300 nm/min	90—100 nm/min	
	Etchant	SiO _x N _y with 7% SiO ₂	SiO _x N _y with 50% SiO ₂	
	1:1 BHF	~35 nm/min	~500 nm/min	
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In wet etching, the etch rates can often vary widely, no matter how well known a recipe is. HF and H_3PO_4 are well-known etchants. But even then, different labs get slightly different numbers because of the variation in the film qualities. Thermally grown silicon dioxide is of good quality, but relatively. SiO₂ grown in the Intel fab can be of a higher quality than in an academic lab, leading to a change in the etching rate. Often, people say I deposit or etch SiO₂ and provide the etch-rate, but the details of the deposition process are hidden or often not reproducible. You may deposit SiO₂ using PECVD. Under various conditions of PECVD, you get different types of SiO₂, which will change the etching rate. You can expect a higher etching rate in an unregulated hot clean room than a colder lab at a higher latitude.

The impurities in the layer are also significant factors. While looking at the contamination policy, we discussed that we have to very careful about the contaminants while doing deposition. Each tool allows a subset of impurities, which decides the impurity levels. Since this is an electrochemical process, even the trace impurities can change the etching rate. Here are two examples to highlight it.

The etchant is 1:1 BHF. If you etch PECVD SiO₂ deposited at 450°C, you get an etching rate of around 300 nm/min. Compare this to a high-quality thermal oxide grown at 1100°C, which will have an etching rate of only 90 - 100 nm/min. That is a vast difference (a factor of three), even though chemically, both are SiO₂. Another example is of the impurities. In this case, imagine you want to etch a silicon oxide nitride alloy. A 7 % SiO₂ and 93 % Si₃N₄ would etch at 35 nm/min, but for the same etching with 50 % SiO₂, you get an etching rate of 500 nm/min. The trend is understandable. HF etches the film with more SiO₂ faster. But the change is humongous – for a 7 % to 50 % change in composition, the etching rate changes more than an order of magnitude. So, you have to be a little careful when you are talking about wet etching.

This variability and poor controllability led people to move towards dry etching in semiconductor fabrication. Dry etching tends to be a little more reproducible.

Feature	Advantage (+)	Disadvantage (-)
Wet etch processes are generally isotropic	Smooth wall profiles	Poor side wall control Useful only for non-critical features
Etch rate varies with temperature, concentration, etc.	Large design space	Poor process control
Wet etch processes can be highly selective	Can do deep etches	
Liquid phase reaction	Easy to do	More particulates Drying leaves stains Surface energy issues

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Let us discuss the characteristics of wet etching, especially the advantages and disadvantages vs. dry etching. In general, the wet etch process tends to be very isotropic because it is hard to find chemicals with a very profound change with crystal orientation, and diffusion plays an outsized role.

The advantage is that you get very smooth wall profiles (because of diffusion and other factors). Anisotropic etch tends to give a rough shape. The disadvantage is that you have poor sidewall control. As semiconductor fabrication features became smaller and

smaller, wet etching has become out of favor because it is tough to maintain the small openings you are trying to make. Photolithography engineers worked so hard to reduce the gap to $< 1 \ \mu m$ or $< 100 \ nm$. Whenever you do a wet etch, those holes widen, which wastes resources and effort. The sidewall control is also low. It is not just criticality of the feature; sometimes, you need vertical walls. You may be doing a microfluidic experiment where you don't want a hemispherical shape but a 90° cross-section. It is challenging to get using wet etch. If you are making a photonic circuit, the waveguide effectiveness changes depending on whether you have a hemispherical or a rectangular cross-section. Rectangular cross-sections are preferred and are not possible with wet etching.

The etching rate varies with temperature and concentration. The advantage is there is large design space. If you spend time and effort, you can identify the conditions at which the wet etch does something. The problem is those conditions are difficult to meet. The range of variation that you can tolerate is so small that for practical cases, it is impossible to hit every single time. So, run to run, day to day, month to month repeatability are all very low.

The wet etch process can be highly selective. We will discuss an example in the next lecture. It is not hard to have a selectivity of 10^4 :1, 10^6 :1. For example, with silicon dioxide and silicon, silicon does not etch at all. The selectivity is nearly infinite, and that allows you very deep etching for thin masking layers. Even if the photoresist is only a micron, you can go very deep in silicon. In dry etching, that can sometimes be an issue.

A significant advantage of wet etching is that it is a liquid phase process. You take a wafer, put it in a beaker with liquid, and the etching happens. A student can learn etching within a day. It does not require infrastructure, is cheap, and very easy to handle chemicals. If you compare this to CVD, where we have to manage gases, have detectors, complex pumping systems, wet etching is far simpler. When you move from wet etching to dry etching, you once again have vacuum chambers and plasma. The design and control of the plasma become complicated and more expensive. A dry etching system is worth crores; hood to do wet etching is worth a few thousand. The disadvantage of the liquid phase reaction is more particulates. The gases can be much purer than liquid. It is tough to get 6N liquids, but easy to get 6N gases.

You also form particulates while working with liquids. Any small amount of particles in the ambient get into the liquid and form a layer, and stick to wafers when you take them out. Drying becomes tricky, as we discussed during cleaning. I emphasized that you have to be very careful in drying a wafer after cleaning; otherwise, you get coffee stains. It is true even for etching; if you are not careful, you form coffee stains that can create problems later. Wet etching tends to do that because there is always contamination and byproducts in the solution. When you take the wafers out of the solution, some of that remains. You can never completely get rid of it.

There are surface energy issues, too, especially when you are looking at critical dimensions. Often liquid does not wet tiny features and cannot penetrate a nanometer feature and hence, is unable to etch. These problems go away in the gas phase and plasma.

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Let me take a step back and talk a little bit about safety. Many chemicals used in the semiconductor industry, like HF, HCl, or sulfuric acid, etcetera, are remarkably dangerous. The industry has stringent standards about the use and disposal of the chemicals. You must follow those for your and environmental safety. We mandate that you always wear an apron, chemical goggles, face shields, long sleeve, lab coats, closed toes, and gloves when you use wet chemicals in our cleanroom. These are non-negotiable.

There are different gloves; many users have access to thin nitrile gloves that you can buy cheaply from a market and use for examination. However, they are not suitable for corrosive chemical usage or hydrofluoric acid usage, but only for general purpose, handling of wafers, solvents, or biological samples. For aggressive chemicals such as HF, sulfuric acid etcetera, please invest in thick nitrile gloves (2 to 4 mil thick) rated for acid, bases, and toxins. Cryogens have nothing to do with wet etching, but again if you are doing cryogenic work, use appropriate gloves. Different gloves are suitable for different things; there is no single glove that protects you from everything.

For wet etching work, especially in semiconductors, I would strongly recommend not using latex. Latex gloves are cheap but not good because they are permeable. Vinyl gloves are actually for the food industry so that people who are cooking do not contaminate the food, but they are not suitable for chemicals and won't protect you from chemicals. Do not use fabrics or things that create particles. Asbestos has an added problem; it is carcinogenic. So, please do not use asbestos.

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Hydrofluoric acid is probably the most dangerous acid inside a clean room, and we must respect it. It is dangerous partly because it is odorless, colorless. It looks like water, has the viscosity of water, and we often use a dilute HF solution, which is mostly water, but it does not take a lot of HF to cause damage. You need to expose your body at 1 %, Just a small area on your body is enough to create a potentially toxic or life-threatening exposure. One drop, a little bit of spill, is enough to cause a lot of problems. And the worst part is, a lot of times, exposure initially is painless. You do not even know. That is why personal protective equipment is so essential. They make sure that even inadvertently, you do not get exposed. If you do, harmful things can happen. For example, you can get decalcification of the bone, the tissue underneath can start dying. These are very excruciating, painful things.

When you use the HF, you can get exposed without realizing it. You go home, sleep, and at night, wake up to the excruciating pain. For exposure to 20 %, there are no immediate symptoms, making it very dangerous. If you see any of these symptoms, please contact your health center immediately. If you know about the exposure, you can quickly treat it by rubbing calcium gluconate gel if it is recent. If you are using HF in your lab, please store calcium gluconate gel, a lot of it. If you ever have HF exposure, please put it immediately. In the next lecture, we shall look at more etching recipes and discuss wet etching further.

Thank you.