Fundamentals of Micro and Nanofabrication
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Lecture – 05
Contamination and surface cleaning

This is Fundamentals of Micro and Nanofabrication. My name is Sushobhan, I am from IISc, Bangalore and today we are going to talk about cleaning recipes.

In the last lecture, we looked at what is a cleanroom, why do we need a cleanroom, what are the various techniques we use to keep clean rooms clean of particles and chemicals so that contamination does not fall on top of our wafer. However, contamination does always fall because practically no matter how clean a cleanroom is there are always particles. We need to find a way to remove those particles and chemical contamination before critical processes, and that is the subject of this lecture.

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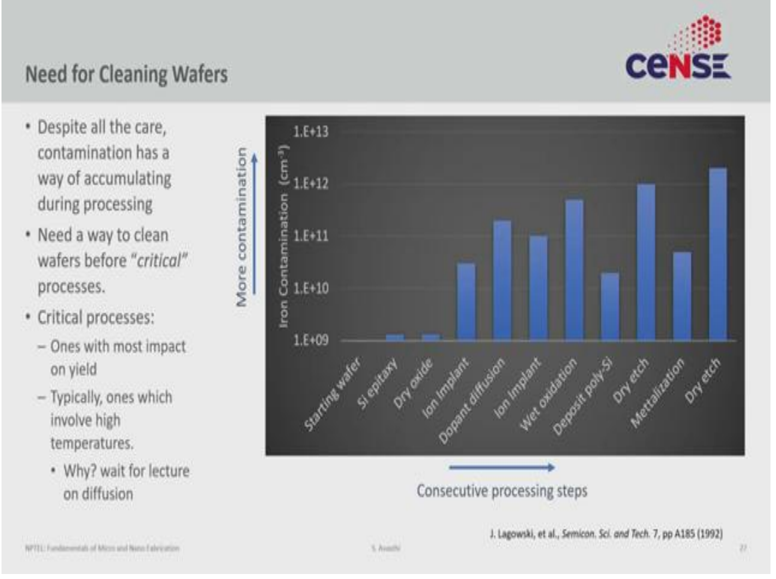

This is an example of a study that was done to track contamination on top of wafers. So, you start with an extremely pure wafer. However, as you do consecutive processing steps on it, as you make a device on it, by the time you get to the end the number of particles on the surface accumulates. This is a known problem that faces any fabrication step. So, before a critical step, you have to find a way to reduce this contamination. Now, what is a critical step? A critical step is any step in a process that has the maximum impact on

yield. Any process that reduces your yield is a critical process. Typically, these tend to be high-temperature processes. Why that is, is better understood when we discuss diffusion.

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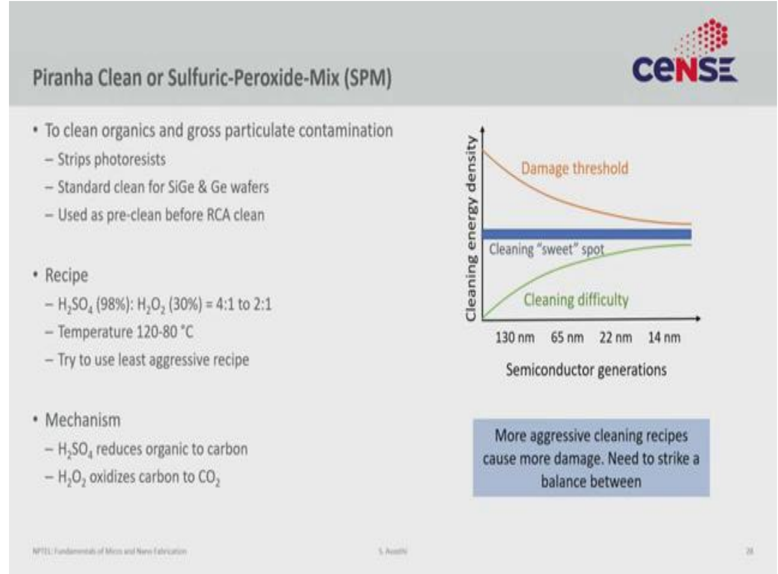

So, how do we do the cleaning? There are several recipes or chemical mixtures that are used to do the cleaning of wafers. Most of this lecture is focused on silicon because it is the workhorse, though we will also touch on what cleaning other substrates can use. A lot of time the other substrates also tend to use the same techniques and chemicals, so it is illustrative to understand how silicon cleaning works.

Let us first look at piranha clean, also called sulfuric peroxide mixture, SPM. It is a mixture of hydrogen peroxide and concentrated sulfuric acid. It is used to clean organics and gross particulate contamination and also strips photoresists. It is a standard and primary process for cleaning Si-Ge wafers because Si-Ge wafers are not compatible with the next clean we going to talk about. It is also used as a pre-clean before the RCA clean.

The recipe: take concentrated sulfuric acid (98 % sulfuric acid in water), H_2O_2 (30 % H_2O_2 in water) and mix in a ratio of 4:1. In the semiconductor world, the molarity and other sorts of concentration measures are not popular. People typically give you recipes in these 1:2, 4:1 type of ratios that mean: for 4:1 mix, you take 98 % sulfuric acid 4 parts and 30 % peroxide one part and the mix the two. This is the common way specifications

are given, partly because we are electrical, electronic engineers and material scientists; we are not chemists.

The temperature of the mixture is often kept at 80-120ºC. In general, use the least aggressive recipe. Any cleaning recipe is also an etching recipe as you are trying to etch the contamination on the top, but that etching may also etch the silicon or the structures fabricated on top. In this curve, the cleaning energy density is plotted against the technology node (smallest feature size). The damage threshold is the energy density of the cleaning solution above which you will start causing damage. The cleaning difficulty curve is the minimum energy density needed to clean in the first place. The difference between these two curves is your operating range. Your cleaning methodology needs to be within this range where it does not cause damage but still does the cleaning.

And as the semiconductor generations have progressed the distance between these two curves has become narrower because the structures are flimsier, making this window narrower. As much as possible remain closer to this green curve (not very aggressive cleaning, the most dilute version of the cleaning solution).

What is the mechanism of this clean? H_2SO_4 is an oxidant that dehydrates organic matter to carbon that then gets oxidized by H_2O_2 into carbon monoxide or carbon dioxide which leaves the solution, thereby removing the organic contamination.

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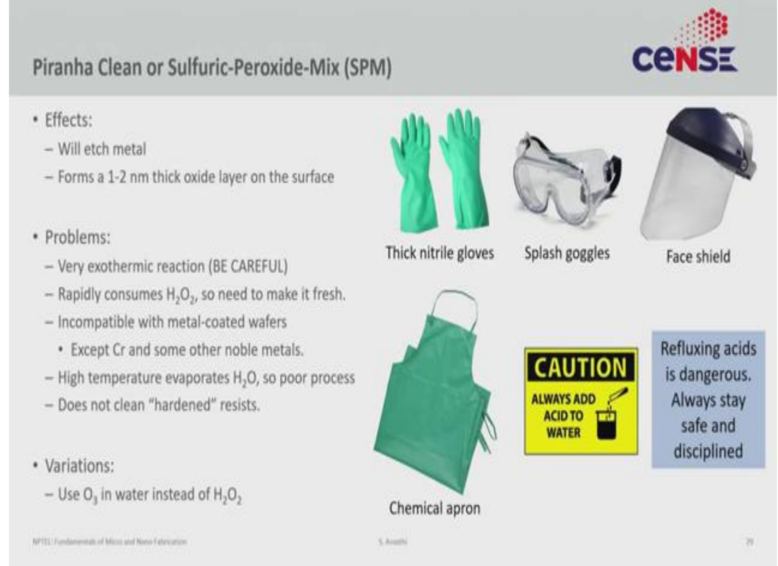

There are certain side effects of the piranha etch or SPM etch. It will etch metal so do not do piranha clean on samples that have metal on them. It also forms 1-2 nm thick oxide layer on the silicon surface because the silicon gets oxidized by H_2O_2. It is a weak quality oxide, called the chemical oxide which is not useful for any electronic application but does form. It also is a very exothermic reaction. So, you have to be extremely careful. In fact, the solution tends to be self-heating. Even if you do not heat the beaker or the bath extrinsically, just by the virtue of mixing peroxide and sulfuric acid the whole solution will heat up to 80-120°C. The larger the batch, the more heating. This mixture rapidly consumes H_2O_2 as it releases the oxygen. So, you need to make this a fresh solution every single time. You cannot make a batch and then keep it over a week. It has to be made fresh, right, before the experiment (half an hour to one hour).

It is incompatible with metal-coated wafers but there are exceptions like chromium and other noble metals that do not react with sulfuric acid. In those cases, you can use this clean. The high temperature evaporates water, so the concentration of sulfuric acid changes in the system, so the process control is not very good. And it also does not clean very hardened resists; The word hardened will be better defined when we discuss lithography and etching. There are some modern variations of this, where people have started using ozone instead of H_2O_2, for cost reduction, better control etcetera. We will discuss it later.

This is a very aggressive chemical mixture, more dangerous than sulfuric acid alone. So, you have to be extremely careful in managing this. You always wear PPE or personal protective equipment, which is nitrile gloves, splash goggles, face shields, chemical aprons. Always remember the standard rules such as always add acid to water and not the other way around. This is a refluxing, boiling acid. It is very dangerous, please stay safe and disciplined.

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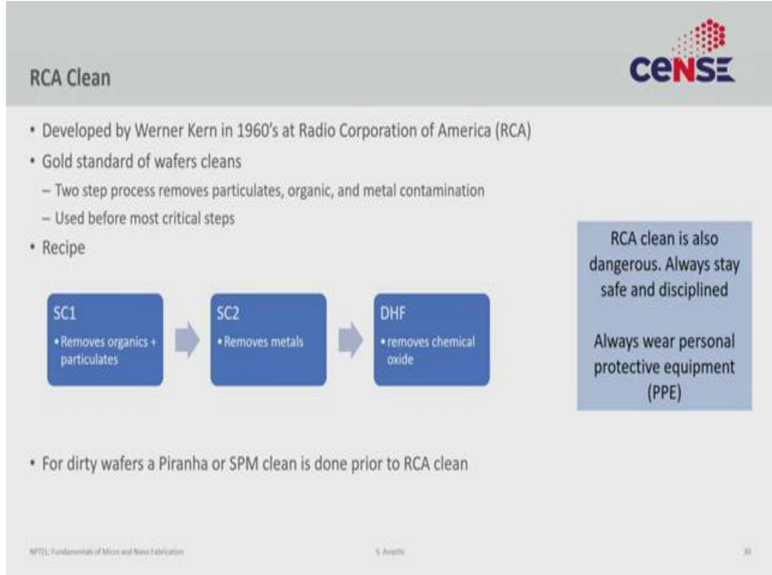

The next is the workhorse that is used in the industry and also in a lot of research labs and universities is RCA clean, developed by Werner Kern in the 1960s. Kern's original paper is available on the internet and is very insightful to understand the thinking behind the developing of this cleaning recipe. It is a gold standard for wafer cleans, which is a 2 step (or 3 steps) process, to be used before all the critical steps in silicon processing.

SC 1 step removes organics and particulates, SC 2 step removes metals and then there is a step to remove the chemical oxide that always forms on the top. RCA clean is also very dangerous. It is more dilute acid, so arguably less dangerous than piranha, but still very dangerous. Always wear personal protective equipment while doing RCA clean. For very dirty wafers often piranha clean serves as a pre-clean for the RCA clean.

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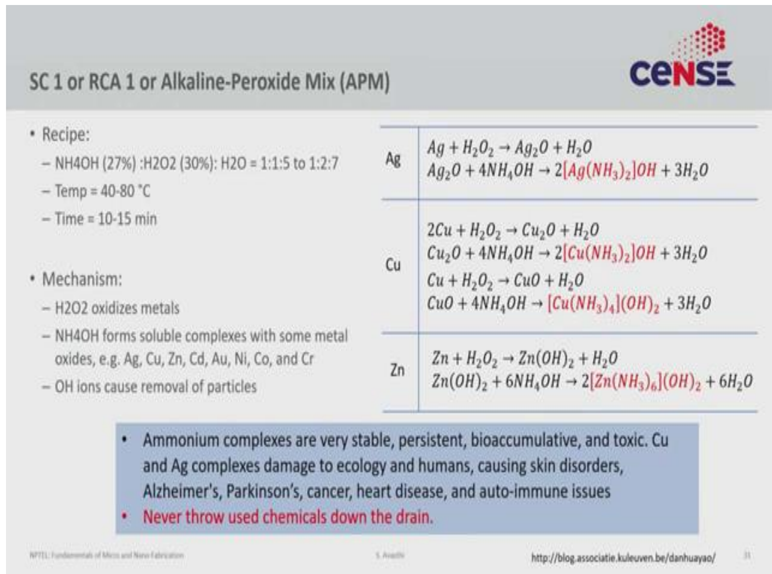

Let us look at SC 1 (RCA 1) or an alkaline peroxide mix (APM) solution. The recipe is NH_4OH (27 % in water), H_2O_2 (30 % in water) mixed in a ratio of 1:1:5 or 1:2:7 or even more dilute versions in some cases. The temperature of the solution is around 40-80°C and does not self-heat as much because there is a lot more water in this, so you have to externally heat it either using a hot plate or through a bath. Typically, you do this clean for 10 to 15 minutes, the same as piranha before.

The mechanism is similar; H_2O_2 oxidizes the metals, NH_4OH forms soluble complexes with certain transition metals such as silver or copper or zinc. Here is an example: silver gets oxidized into Ag_2O that reacts with NH_4OH to form this ammonium complex and ammonium complexes tend to be very soluble. Silver oxide on its own is not soluble in water, but ammonium the ammonium complex is. Similarly, copper oxide is not soluble in water, but the ammonium complex is. The formation of this complex allows you to make a soluble version of this contamination that you can then wash away. Without NH_4OH, the silver oxide would just precipitate on top of the wafer. Even after oxidation, there would be no way to remove it, solubility is the key. There are safety and environmental concerns; ammonium complexes are very stable are very big environmental hazards. They accumulate and persist for a long time and are toxic, especially if you have a lot of copper or Ag contamination and you are using RCA to remove it. Whatever you form, needs to be treated as a hazardous waste, it should not be thrown away down the drain, the water supply or the sewer as it will cause things like

Alzheimer's, Parkinson's, cancer, heart disease, and autoimmune issues. It is a very bad chemical to throw in the environment. So, please refrain.

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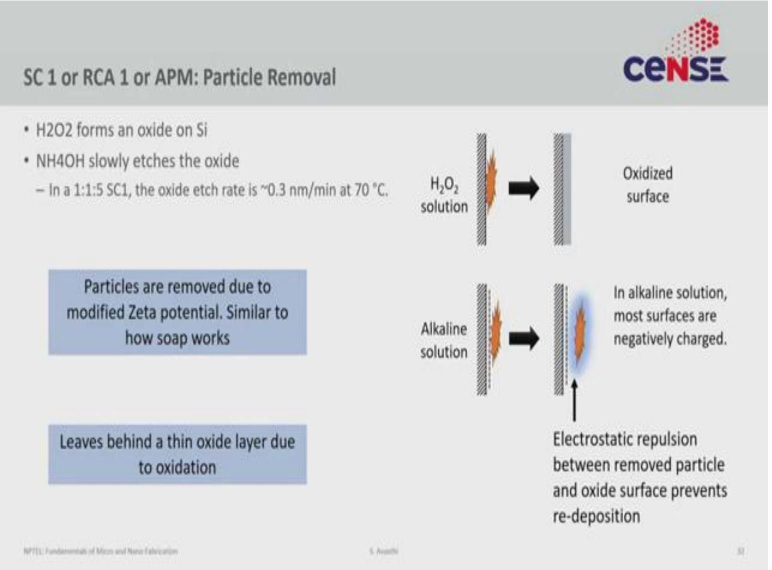

OH^- ions also help in removing the particles. This is a basic solution; it removes particles very similar to how detergent or soap removes particles from your body. Either the particle gets oxidized with the H_2O_2, in which case you just chemically convert it off or the particle remains in its form, but then the zeta potential of the surface energy of the particle changes because of the OH^- ions and there is electrostatic repulsion between the surface and the ion and the particle goes away. This is exactly the same way the soap works or how certain basic solutions are used to clean glass.

A side effect of SC 1 is that you leave behind a thin layer of oxide on silicon because of H_2O_2.

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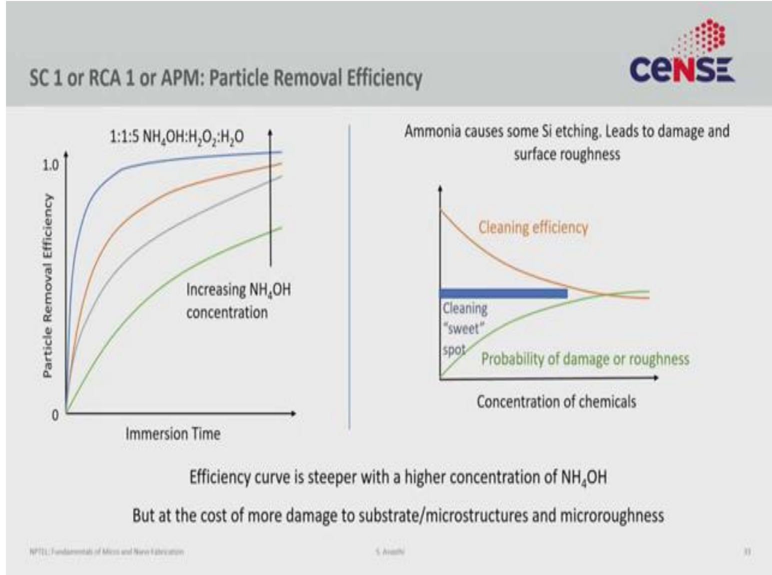

The particle removal efficiency depends upon what dilution you are using. The more aggressive solutions tend to be better removing the particle; however, you have to be careful because as you increase the concentration of chemicals, the probability of damage or roughness increases and at the same time the cleaning efficiency reduces and again you are looking at this sweet spot in the middle. You have to play with different concentrations; start with the lower one, go higher if it is not getting cleaned.

Ammonia causes some amount of silicon etching, as it is a base and basic solution etch silicon, leading to damage to very small features and might also cause micro roughness. Even though you start with a smooth surface, if you leave it in ammonium hydroxide it will start to roughen up. That can be prevented by going to lower concentrations but at the cost of poor cleaning.

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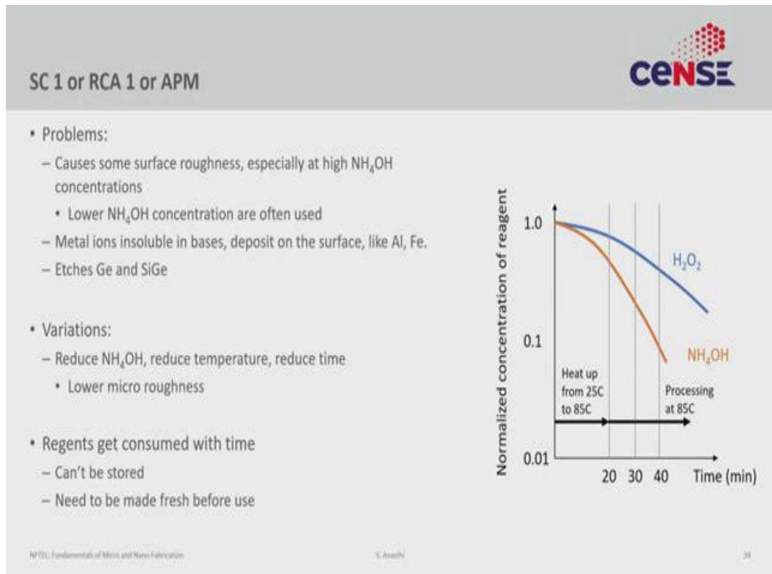

Just like the piranha, APM solutions also degrade with time. If you look at the normalized concentration, within 40 minutes or so, only 10 % of the solution remains. The only way to do this is to make a fresh batch every single time. It takes a certain amount of time to just heat up the solution to around 80ºC, then a 10-20 minute window in which you can use the solution after which it is spent. You cannot make it or store it in advance.

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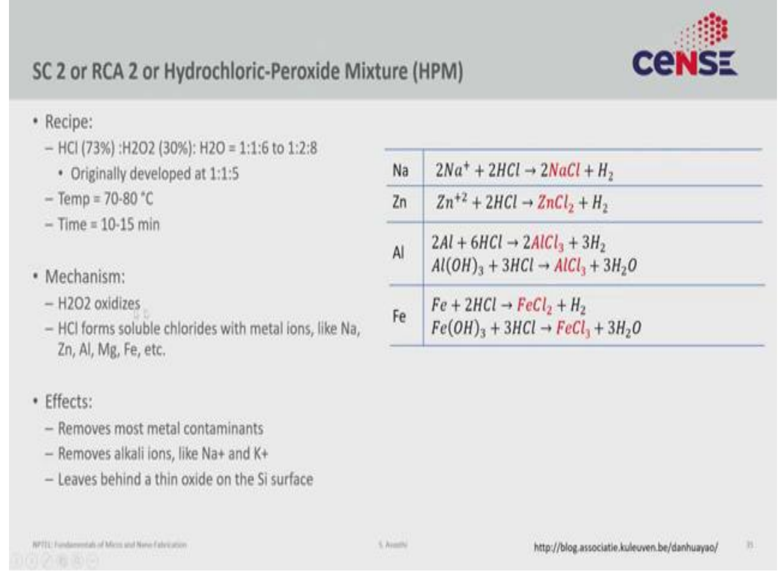

The other next step in the RCA clean is SC 2 (RCA 2), a hydrochloric - peroxide mixture (HPM). Just like the previous one, it has hydrochloric acid, peroxide, and water in 1:1:6 or 1:2:8 ratios, where instead of ammonium hydroxide, you have HCl (73 %). You heat this to around 70-80°C and leave it in the solution for 10-15 minutes.

The mechanism is similar. It is just an acidic solution instead of alkaline. H_2O_2 oxidizes, then HCl forms soluble chlorides. Sodium or zinc or aluminum or iron impurities react with HCL to form chlorides are very soluble. Just by washing the wafer later, you can remove this contamination from the surface. This also leaves behind a thin layer of oxide on the silicon surface because of H_2O_2 just like the previous two cleans.

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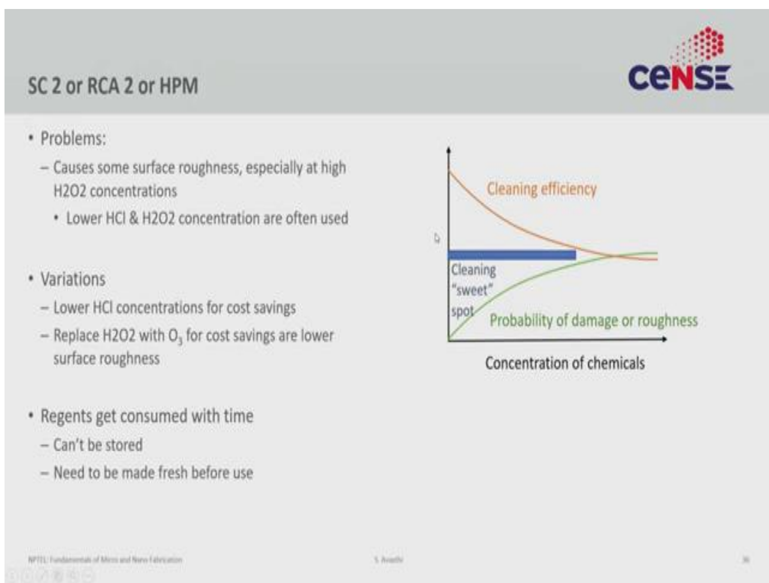

What are the problems? surface roughness, especially at high H_2O_2 concentrations. There again is this tradeoff between cleaning and probability of causing damage and you want to be in a sweet spot. The industry has for cost savings and other reasons tried to migrate toward lower concentrations of HCl and replace H_2O_2 with ozone. The reagents get consumed with time so you cannot store it but have to make it fresh before use.

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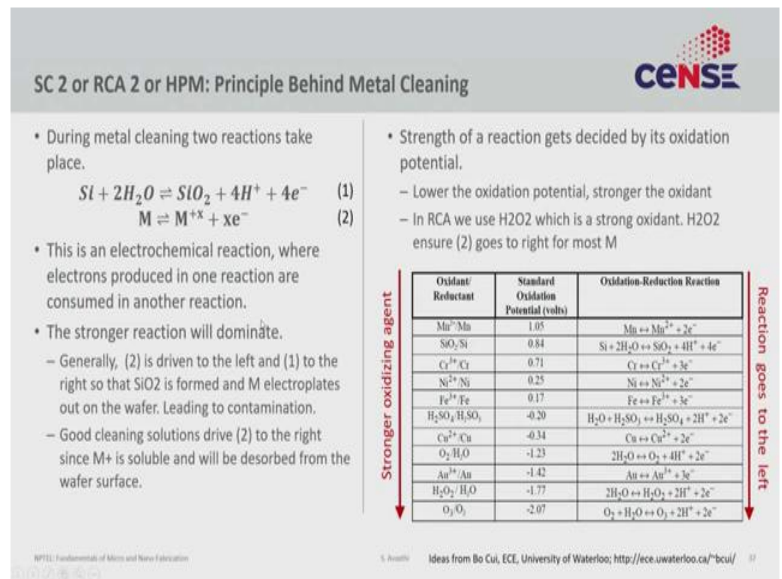

A little bit more about the mechanism behind the HPM clean. On the silicon surface, there are two things that can react; silicon can form silicon dioxide and metal will form the metal ions. So, there is an electrochemical reaction depending on the standard oxidation potential of the impurities. In general, if you do not have any other reagent in the solution, reaction 2 is driven to the left - the metal plates out and reaction 1 is driven to the right - the silicon oxidizes because it has a tremendous tendency to oxidize. Silicon wants to oxidize, and that forces the metal to reduce which is why you actually get contamination.

Now, in order to prevent your metal from plating on top of the surface, you need other reagents (for example, hydrogen peroxide). Hydrogen peroxide has a very low standard oxidation potential, making it a very strong oxidizing agent. An oxidizing agent will oxidize everything that is above it in the standard oxidation potential table; gold, copper, iron, nickel, chromium, and silicon will get oxidized. However, things below it will not but that is not a concern for most metals as H_2O_2 will oxidize most of them. This oxidation pushes this reaction to the right and then that iron can react with the chloride to form a soluble complex that can be then washed away. This also tells what sort of oxidation agents would be good. It is good to use H_2O_2, it might be better to use ozone because it is a stronger oxidizing agent and that is why the industry is trying to move towards it. Several ideas and the slide come from Professor Bo Cui's (ECE Waterloo) lectures which are very illuminating.

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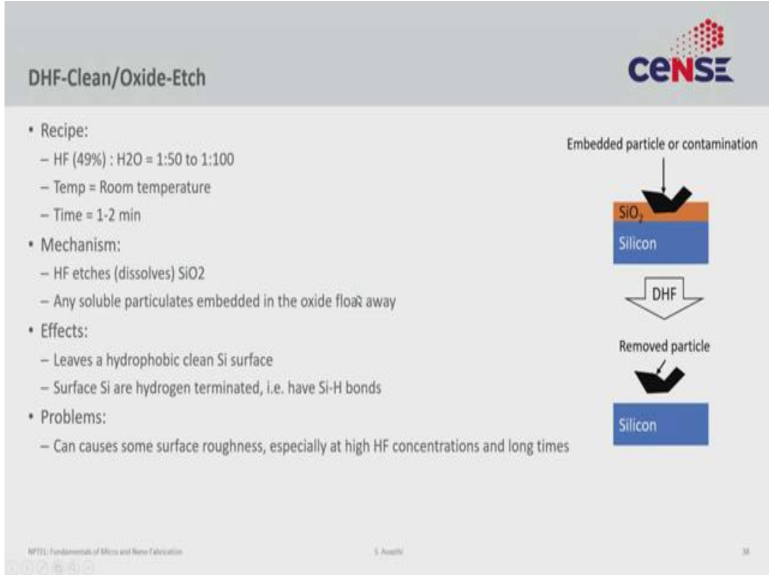

The last step and an optional step: chemical oxide removal. Chemical oxide forms on the surface because of the ammonium hydroxide, sulfuric acid or hydrochloric acid step. This step is typically done with a dilute (1:50 to 1:100) solution of hydrofluoric acid in water at room temperature and it takes only 1-2 minutes depending upon the concentration. Particle contamination embedded in the silicon oxide may go away with the oxide when you put it in the hydrofluoric acid. The problem is it again causes micro roughness. This step should be done in as dilute solution and for as short time as possible. As a side effect, it leaves a hydrophobic surface on which the water does not stick. If you take the wafer out, you will see no droplets on it because the water does not stick to it. That is a sign that the etch has completed. It also passivates the surface of the silicon with silicon hydrogen bonds.

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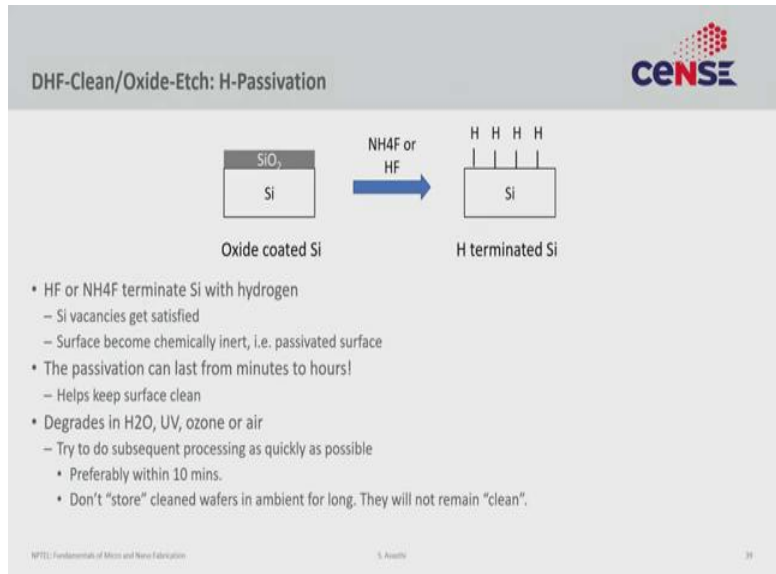

Once you remove silicon dioxide through ammonium fluoride or hydrogen fluoride, you form the Si-H bonds on the surface that passivate the surface chemically and electronically. The downside is that it just lasts from minutes to hours as ultimately the oxygen from the ambient will react with Si-H bond and form silicon dioxide again. Practically, what it means for the cleaning step is that the cleaning must be done before the critical step, and the time between the cleaning and the critical step must be kept as low as possible because this hydrogen passivation allows the surface to remain clean, and but with time it will degrade and once it degrades you tend to re-accumulate the junk on the surface. A good rule of thumb is that the time between the cleaning and the step after it should not be more than 10 to 30 minutes.

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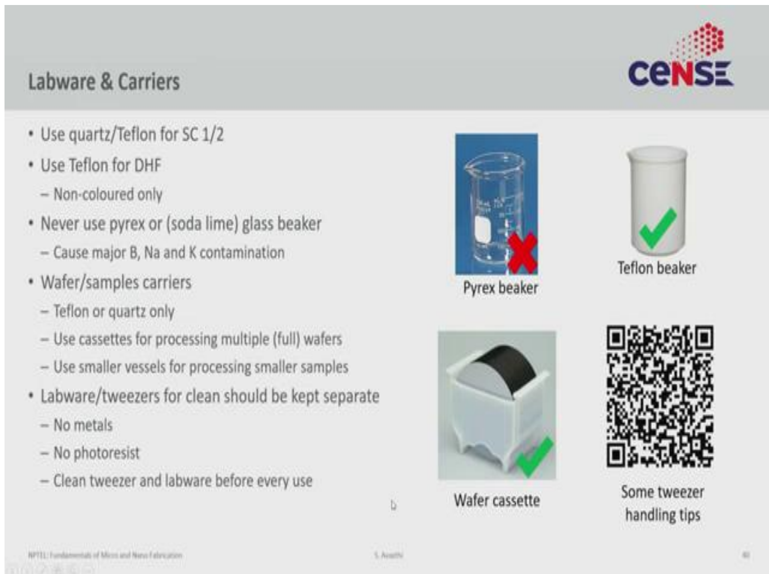

Let us talk about some labware that you must use to do this cleaning. Remember, we are doing this to remove contamination. So, the labware must not introduce unintended contamination. Always use quartz or Teflon labware. Try to avoid colors or pigments, just use virgin clean Teflon. Try to avoid Pyrex or soda lime beakers; they are very cheap, very easily available, but chemically soda-lime glass or Pyrex glass is full of boron sodium and potassium that will cause contamination on top of your wafer. So, please avoid those.

Here is an example of a wafer carrier that allows you to process several wafers at once. For smaller wafers, you can keep them directly into the beaker. We also need some way of manipulating the wafer either a tweezer or wand. Please do not use metal tweezers, photoresists, keep the tweezers clean. Tweezers used to clean the substrate must not be used for anything else, you would always end up creating contamination that will come back to haunt you later. Here is a QR code from a website that actually gives you some tweezers and handling tips. It is very easy to go in buy low-quality tweezers of unknown cleanliness and unknown quality, I would encourage you to use only Teflon or polypropylene tweezers, glass filled Delrin, few other material types. Please do not use metal tweezers, even with Teflon coating as they are not suitable for most applications that require acid or base cleans because over a period of time this Teflon coating comes off and you are back to square one with metal contamination on your wafer. For more advanced cases you might consider using a wand that picks up the wafer using a vacuum.

Never touch the middle of the wafer; only the edges. Do not breathe on the wafer, make sure they are far away from you, do not put them on dirty surfaces, do not touch them with fingers. It is very hard to remove all contamination from a dirty surface.

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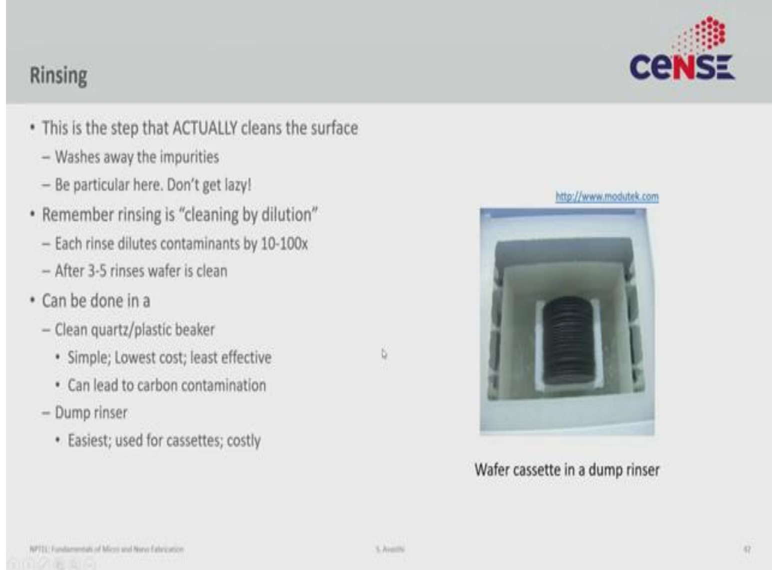

Rinsing: before and after every step cleaning step, there is a rinsing step, but often people do not quite understand how important this is. All the chemical reactions make the contamination soluble, which is still there in the solution. The way we remove that contamination is by rinsing. Do not get lazy in the rinsing; if the recipe asks to it rinse 3 times, rinse 3 times. If the recipe asks to it rinse 5 times, rinse 5 times. Rinsing is just cleaning by dilution. Every time you rinse, the contamination level inside the liquid goes down by a factor (of 5-10x). Rinsing 5-6 times reduces the contamination by 5-6 orders of magnitude.

There are certain automatic dump rinsers that you can use if you have several wafers. They are a little more expensive but available. If you have small pieces of single wafers you can do this in the beaker itself.

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Once you are done with rinsing there is typically a step of blowing dry the wafer. Please note the word 'blow'. The idea is not to dry the liquid on top but to push it off the wafer on to some absorbent cloth. You do not want to dry the water because when you dry the water on a surface you tend to form stains. This is what I call coffee rings. Coffee that dries on top of a table will leave a stain as the solvent evaporates away, the solute just precipitates out on top of the surface.

So, if a liquid dries on the wafer, it will form these sorts of contamination rings on top of the wafer, which is undesirable. We need to push the liquid off without drying it using tools like nitrogen gun or spin dryers.

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A few other wafers do's and don'ts that you may look at in these videos. To summarize it all, always use personal protective equipment, hold the wafers from the edges, never hold the wafer with hand and always blow dry. Make sure that the tweezer doesn't touch the device; hold the small substrates from the edges. Any die once touch by hand will always have sodium-potassium contamination which is not good for the device.

In the next lecture, we will look at some more advanced cleaning techniques. See you next time.