Fundamentals of Micro and Nanofabrication
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Lecture- 06
Advanced cleaning techniques

Hello! This is Fundamentals of Micro and Nanofabrication, my name is Sushobhan Avasthi and I am from IISc, Bangalore and this is the concluding part of a three-part series on surface cleaning. In the first part we understood what is a fab, what is a clean room, why do we need a cleanroom. In the second part, we discussed some basic techniques on how to do surface cleaning, how to handle wafers, tweezers etcetera. And in this third and the concluding part, we will look at some advanced cleaning techniques and the direction in which the industry is going as far as cleaning the wafer is concerned. Let us get started.

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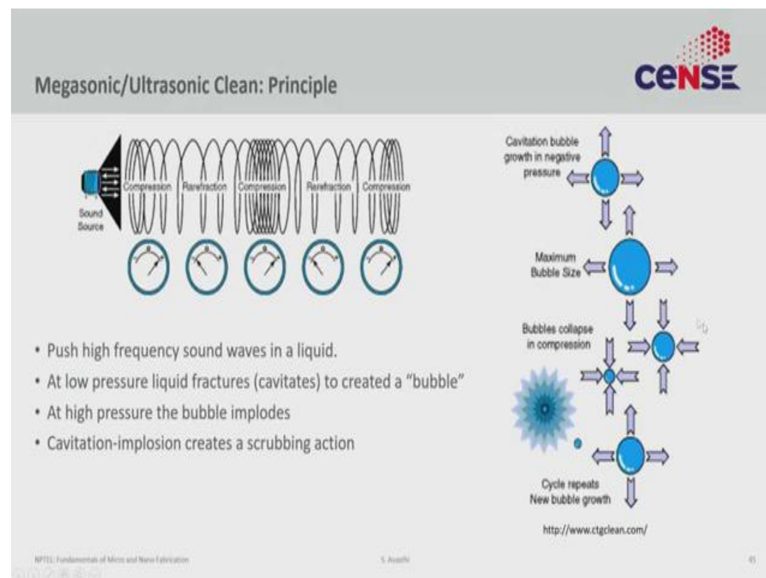

The first advanced concept I would like to highlight is megasonic/ultrasonic clean. Till now, we have only been using chemical energy to do the clean and that is because particulate contamination is very hard to remove mechanically. However, as a secondary effect mechanical energy can be useful, it would be nice to have some sort of scrubbing action that would further help in the removal of particles from the surface. However, a simple scrub would not work very well because (a) it would cause damage and (b) it

would be nonuniform and uncontrolled. The industry uses megasonic and ultrasonic cleaning as a way to impart mechanical energy and certain scrubbing action on top of the surface.

Here is an example of how that works; a sound wave is a pressure wave with successive compression and rarefaction. Putting a speaker right next to the liquid, you would form these waves in the liquid. Imagine a bubble inside the liquid that will contract under positive pressure (compression) and expand in size under negative pressure (rarefaction) and this will happen at the same frequency as the excitation. High-intensity sound waves can actually cause cavitation (generation of small cavities in the liquid) and when that bubble collapses, a significant amount of energy is released. Think of it as a mini-explosion inside the liquid, that is happening everywhere and that mechanical energy can be used to clean the surface.

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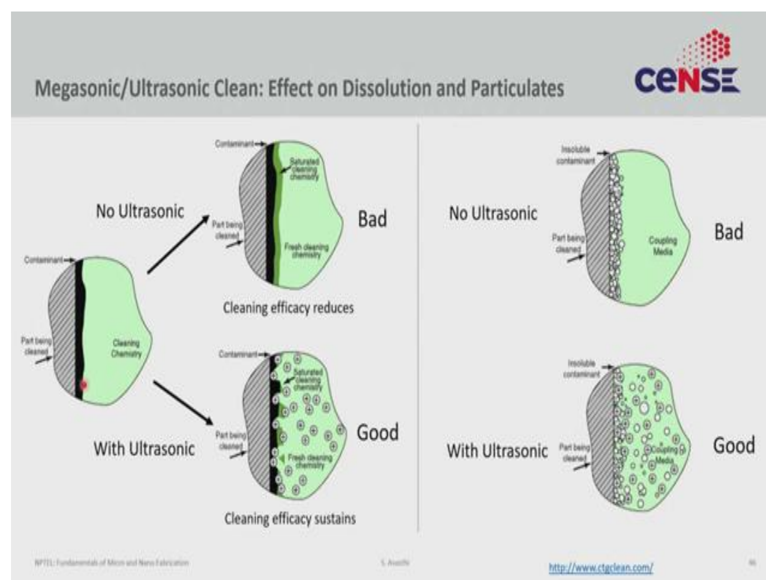

For example, this surface has some crud, shown by this black line and some cleaning chemicals (any of the chemicals that we have talked about). Without ultrasonic excitation, you have a saturated dead layer (boundary layer) on top of this contamination. The only way for this contamination and the solution to react and the contamination to leave the surface is through diffusion. With ultrasonic agitation, the extra mechanical energy can break this boundary layer and improve the penetration and mixing of the cleaning solution with the contamination layer.

This is how ultrasonic agitation improves the efficacy of the cleaning. Ultrasonic clean is also useful if you have a lot of particulate contamination. If you have a lot of insoluble particulates on the surface, your coupling media may not be able to remove it, but if you create some agitation, then that agitation might dislodge these insoluble contaminations and remove them from the surface.

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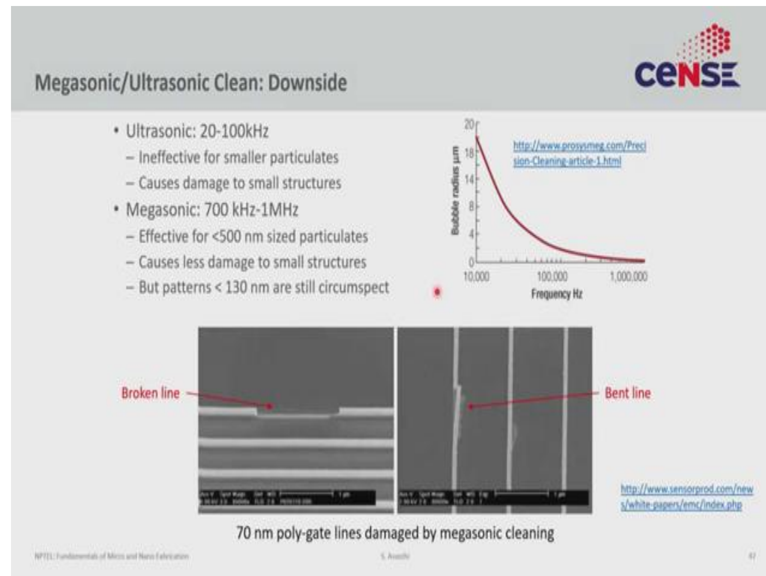

This is the basic idea of ultrasonic/megasonic clean; however, everything comes at a price, nothing comes for free. This mechanical energy can cause damage to the surface, especially if you have very small features. Whether or not the damage will happen depends upon (a) how small the features are and (b) frequency of the cleaning.

Ultrasonic cleaning excitation frequencies (20-100 kHz) are typically ineffective for small particulate. For very small, nano-sized particulates this would not be the best method and also causes damage to small structures (as shown in the curve). The radius of the cavitation bubbles depends upon the frequency; higher the frequency, smaller the bubble radius; smaller the bubble radius more effective the clean is for smaller particulates. To be more effective towards smaller particulates in advance generation fabrication, you need higher frequency - megasonic clean which is around 700 kHz to 1 MHz. It is effective for small particles, but whatever is effective for small particles can also cause damage to small features.

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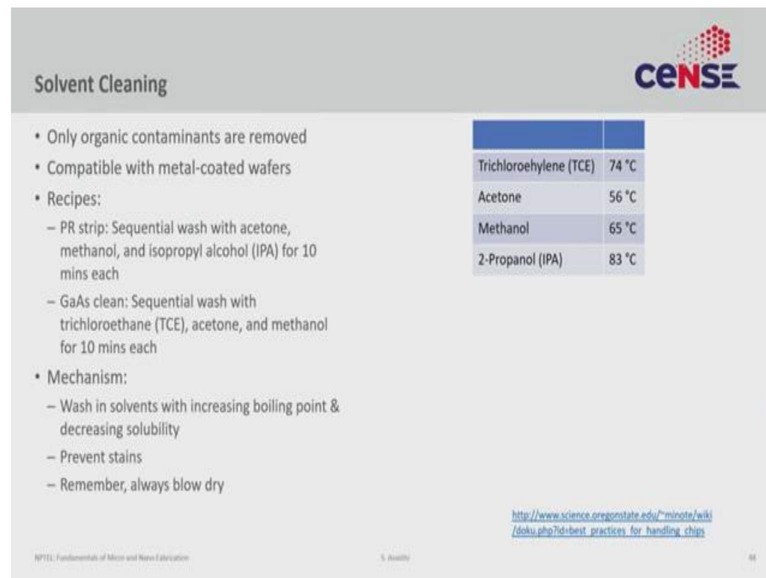

There is a trade-off; you want to remove small particles, but do not want to cause damage to small features. Here is an example of the damage that can happen - metal lines can get broken or bent because of the agitation. You need to be a little careful, especially if you are making very small features.

The last wet cleaning technique that we would discuss is solvent cleaning. We use only organic solvents like acetone, IPA etcetera to dissolve away organic contamination. The contamination can be from multiple sources. The advantage with this clean is that it is compatible with metal, so even if a substrate has metal you can do solvent cleaning but not any of the other cleanings we have discussed till now because they would react with the metal. Recipes often used (for example, photoresist removal) involve subsequent sequential wash in acetone, then methanol, then IPA.

What is the rationale? The boiling points of the solvents have a trend - acetone is the most volatile, then methanol, then IPA. You always go from the most volatile solvent to the least volatile solvent to avoid the coffee stain like contamination. Coffee stains happen when a solvent evaporates and leaves behind a residue. Acetone is an extremely good solvent, but drying acetone is very hard because of its volatility, it just evaporates. If you dip that acetone into methanol and then into IPA, you can now blow-dry the wafer without evaporating it, preventing coffee stains. Hence, this order is important.

Gallium arsenide wafers cannot be cleaned using the aggressive APM, HPM cleans that we have talked about; however, they can be cleaned using solvents. Common gallium arsenide cleaning recipes start with trichloroethylene, then acetone, methanol for 10 minutes each. The base mechanism is very simple; you wash it in a solvent, the organic contamination is soluble in the solvent and goes away. Always blow-dry; you are not evaporating the solvent but pushing it off the wafer.

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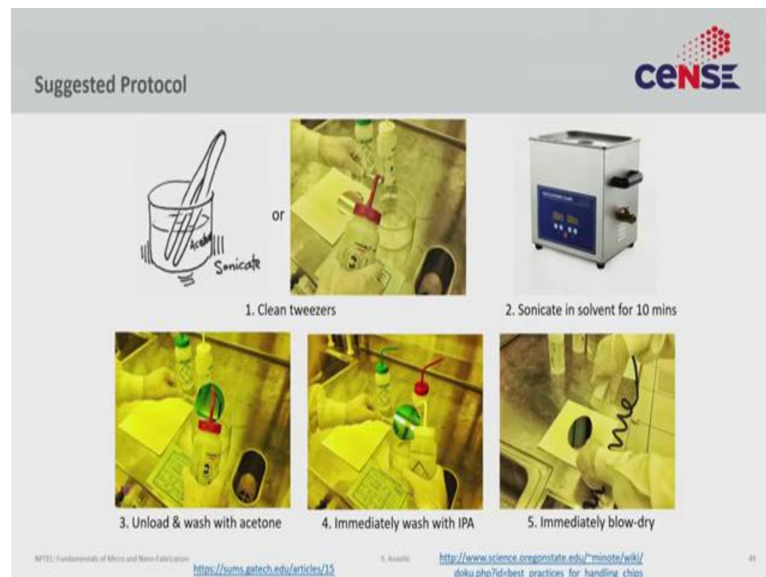

Solvent cleaning protocols: hold the samples with your tweezers properly, use sonication to help and immediately blow-dry. Details of this can be looked at in this very interesting Wikipedia page.

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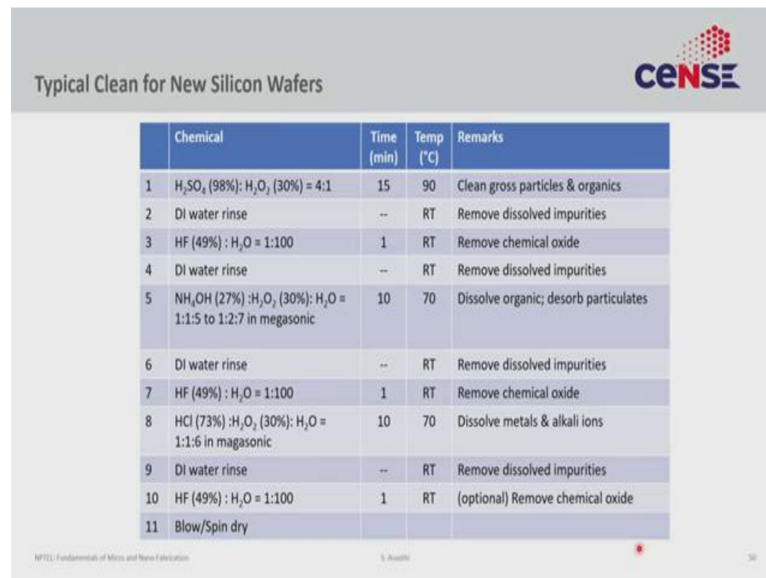

	Chemical	Time (min)	Temp (°C)	Remarks
1	H_2SO_4 (98%): H_2O_2 (30%) = 4:1	15	90	Clean gross particles & organics
2	DI water rinse	--	RT	Remove dissolved impurities
3	HF (49%) : H_2O = 1:100	1	RT	Remove chemical oxide
4	DI water rinse	--	RT	Remove dissolved impurities
5	NH_4OH (27%) :H_2O_2 (30%): H_2O = 1:1:5 to 1:2:7 in megasonic	10	70	Dissolve organic; desorb particulates
6	DI water rinse	--	RT	Remove dissolved impurities
7	HF (49%) : H_2O = 1:100	1	RT	Remove chemical oxide
8	HCl (73%) :H_2O_2 (30%): H_2O = 1:1:6 in magasonic	10	70	Dissolve metals & alkali ions
9	DI water rinse	--	RT	Remove dissolved impurities
10	HF (49%) : H_2O = 1:100	1	RT	(optional) Remove chemical oxide
11	Blow/Spin dry			

Here is a typical clean for a new silicon wafer; start with an optional pre-clean where you do piranha that removes gross particles and organics. You may not need this for a virgin wafer, but if a wafer has been lying around for a long time or you are reusing a wafer you might want to do this step. After that, a DI rinse because remember it is the DI water rinse that actually cleans the wafer. You may want to remove the chemical oxide that has formed by doing a hydrofluoric acid etch and then once again DI water rinse. Next is the RCA that starts with the SC 1 which dissolves organics and desorbs particulates, followed by a DI water rinse to remove the contamination. An optional HF dip to remove the chemical oxide that forms during the ammonium hydroxide process step.

After that, the wafer might become hydrophobic, so you may not need a rinse step because the water does not stick to it. Immediately go to the HPM or SC 2 step followed by DI water rinse. These rinses are extremely important as this is where the cleaning is actually occurring, followed by an optional HF dip and finally, you may want to spin or blow-dry.

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Advanced Wet Cleaning: Ohmi Clean

- Suggested by T. Ohmi (Tohoku University)

	Chemical	Temp (°C)	Remarks
1	O_3 5 ppm in H_2O	RT	Remove organic, carbon & metal
2	HF (0.5%) + H_2O_2 (0.1 to 1%) + surfactant (50ppm) H_2O	RT	Remove chemical oxide, particle, & metal
3	O_3 1 ppm in H_2O in megasonic shower	RT	Remove carbon & adhered chemicals
4	HF (0.1%) : H_2O	RT	Remove chemical oxide. Get H-passivation
5	DI water rinse	RT	Rinsing

More efficient
- Fewer steps
- Room temperature processing
- Fewer chemicals
- Lesser chemical waste

This is what you have to do before the critical steps. The industry has moved towards more efficient cleaning processes that require fewer steps, not as complicated as what we discussed in the last slide. A room-temperature process is important to save time and cost and fewer chemicals because when you are doing this for very large batches, for a long time, the cost adds up because these are extremely pure chemicals and very expensive.

There is also some environmental concern to reduce chemical waste because this chemical waste is dangerous getting rid and very expensive, so that also adds to the cost. In an advance clean that was suggested by Professor Omi from Tohoku University, let's discuss it because of highlights some of the trends in a modern fab. The first thing you notice in the step is there is ozone in water. Ozone is a very easy replacement for peroxide in any cleaning and he has also gotten rid of sulphuric acid completely, which was just an oxidizer to remove organic carbon and metal impurities. Then, HF to remove the chemical oxide, then once again ozone, but this time in a megasonic shower to remove carbon and adhered chemicals, then HF, and then DI water rinse.

So, you have completely removed the requirement for sulphuric acid, hydrochloric acid, ammonium hydroxide, and this works because the modern clean rooms are very clean, they do not have gross contamination, the virgin wafers that you get are very clean and do not have gross contamination and protocols reduce gross contamination. So, these kinds of gentler cleans have become possible and effective.

Several derivatives of Omi clean have come up since then. This slide is a variation using megasonic, surfactants, peroxide, and HF etcetera. In general, the trend is the same: dilute chemicals, lower DI water consumption, smaller footprint, lower energy and exhaust usage and lower cost of ownership.

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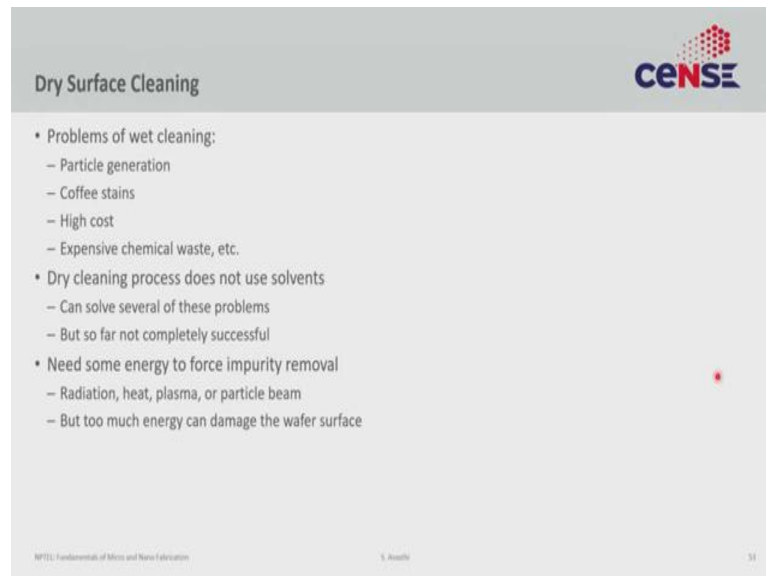

We end wet cleaning and will move towards dry surface cleaning. The concept of dry cleaning is that you do not use liquids at all but use gases or plasma. The reason to do that is with wet clean, you always generate particles because it is very hard to have particle-free chemicals especially, once you start using them they always tend to create particles. Gases, on the other hand, can be particle-free. You always have a coffee stain problem that can be avoided, but not absolutely prevented at all scale. Then there is a high cost because liquids tend to be very wasteful; you use gallons of liquid for 25 wafers and most of the liquid gets thrown away or consumed inefficiently which is costly. You generate a waste which is also very expensive to get rid of and is an environmental and safety hazard. Handling these large amounts of acids and bases and hydrofluoric acids are very expensive.

Dry cleaning tries to solve all that problem by completely getting rid of it by using gases etcetera, but so far it has not been as successful in getting effective cleans and is used in certain niche areas. For critical processes, wet cleaning is still the way to go. How to get rid of liquids? you have to provide the energy to get over the adhesion force right. That

energy can either from radiation (heat or UV), plasma or a particle beam (just mechanical energy from a particle beam). You always have to play that game where you want to clean but do not want to damage.

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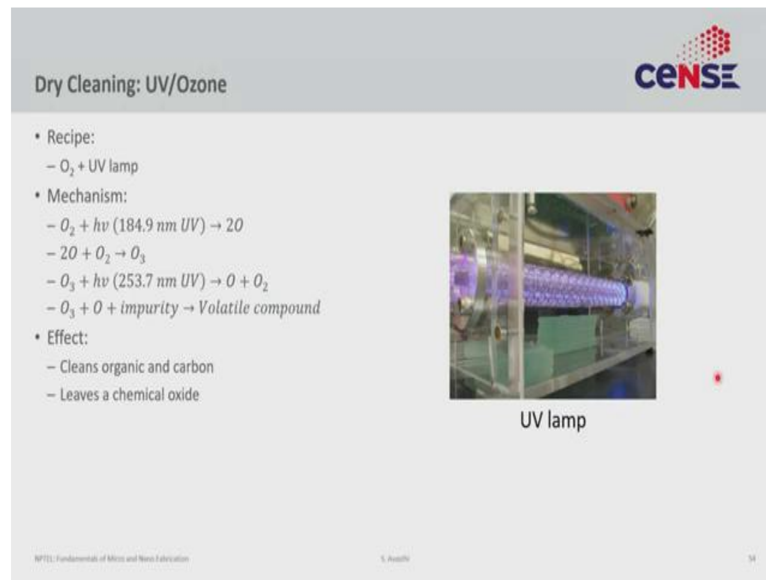

UV-ozone is popularly used. A UV lamp of low enough wavelength will provide enough energy for the oxygen to become ozone. If you take 184.9 nm UV and shine it on O_2, you form ozone that is a very effective oxidizing agent, is volatile and there is no waste it will decompose into oxygen on its own. It removes organic and carbon contamination by just oxidizing and also leaves a chemical oxide.

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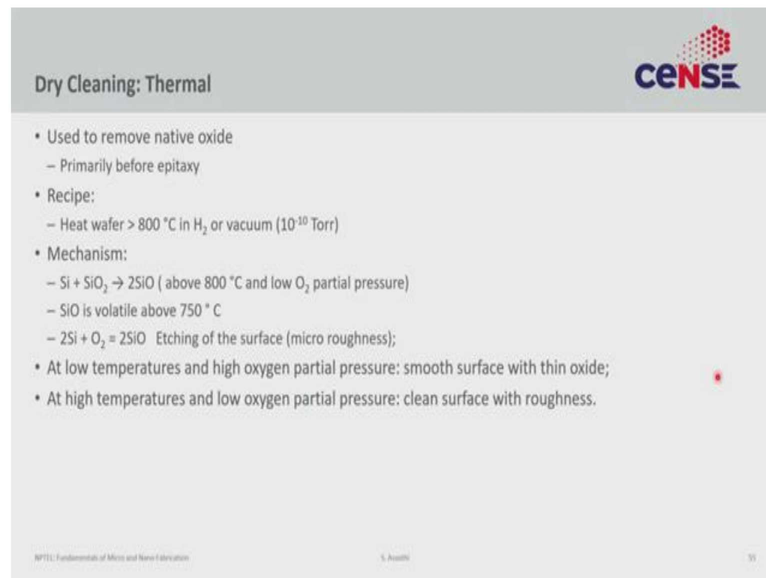

Another dry cleaning is thermal where you take a silicon wafer and heat it to a point where the silicon oxide that has formed on the surface is unstable. Heat the wafer up to 800°C in an H_2 ambient or in very high vacuum (low pressure), which is not very practical for most cases because as soon as you take the wafer out in the ambient and leave it there, the hydrogen passivation goes away and you get silicon dioxide on top again.

The place where this is used often is the epitaxy. If you are growing silicon on silicon and you do not want any SiO_2 at the interface, then you would do this clean before your growth. At high temperature and low oxygen partial pressure, you get a clean surface, but also surface roughness. Some surface reconstruction happens when you heat these things up at high temperatures. You have to play a careful game.

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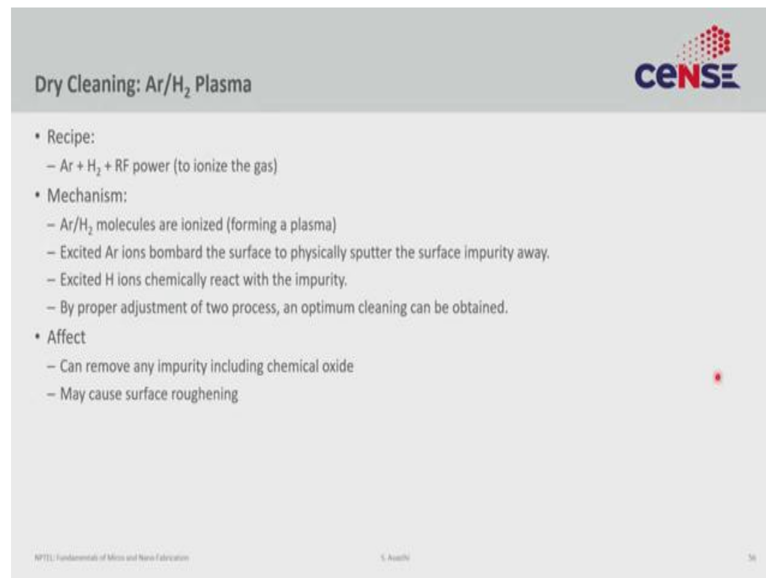

The third dry cleaning method is to use the shower of particles. Take argon or hydrogen which for silicon is relatively inert and create plasma using RF power. Hydrogen forms silicon hydrogen which is not electronically active. And then force this plasma on top of the surface. Plasma has certain energy and temperature that is used for cleaning and dislodging particles and contamination. The problem is surface roughening because this bombarding of ions is not just on top of the contamination, but also on top of the silicon.

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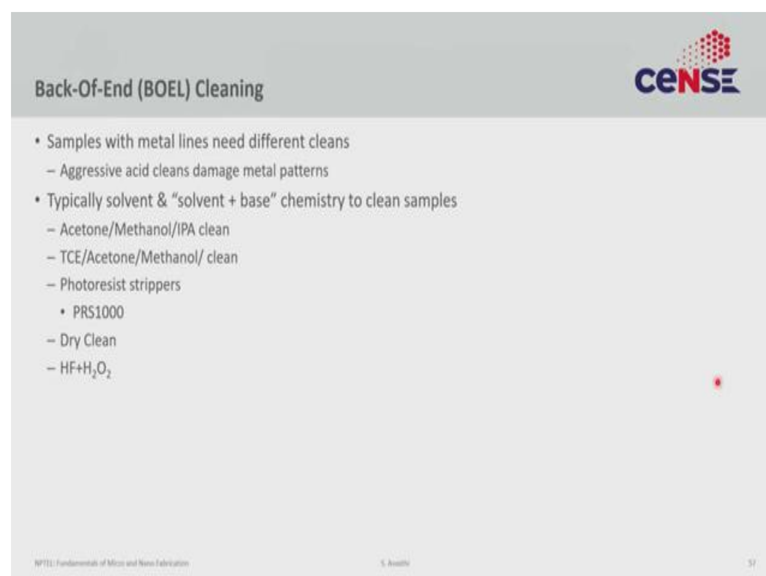

Finally, some back end of the line (BEOL) cleaning. In typical processing, you start with pure and the cleanest tools and then go towards the dirty tools (contamination protocol). Similarly, in the process flow, you start with the steps that are the most critical steps that require the highest purity and do all the metallization towards the end. Once you have deposited metal on the top, you are in the back end. Towards the back end of the line processing, the recipes have to allow metal so the standard RCA and piranha etcetera are not useful. You need to have recipes that tolerate metal and one that we have discussed is solvent cleaning. You also can use some customized liquids such as photoresist strippers, certain types of dry clean, for example, argon plasma can work. Dilute versions of HF/H_2O_2 are also used to do some of those cleanings. One BEOL clean that we would go into detail is this HF/H_2O_2 mixture. It is typically used to clean the dielectric film. In semiconductor towards the end, you have multiple metal layers and each metal layer is separated by a dielectric and before the deposition of a new metal layer you need to clean the dielectric that is underneath.

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BEOL Cleaning: HF/H_2O_2

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- Used to clean dielectric films with exposed metal patterns
- Recipe
  - Step 1: HF (600 ppm) + surfactant + H_2O_2 (0-0.5%)
  - Step 2: O_3 (5ppm)+ H_2O
- Mechanism:
  - HF barely enough HF for particle removal
    - Any more and it will etch too much of dielectric
  - H_2O_2 to control etch of the metal layer
    - Exact concentration depends on the metal
  - Surfactant
    - For controlling surface energy, i.e. wetting the surface
  - O_3
    - Remove surfactant residue

And the way you do that is to add HF, surfactant, and H_2O_2 in low concentrations and that cleans up the dielectric surface and in the second step, flow ozone and water to just remove any of the contamination sticking on the surface. The mechanism is very similar to what we have already seen, HF is used to etch the dielectric a little bit and H_2O_2 to control the metal layer etch. The exact concentration depends on the metal and details. Surfactant is there to tune the surface energy.

Similar to how detergent is used to tune the surface energy while cleaning the cloth, surfactants in cleaning liquids control the surface energy while cleaning wafers. Finally, ozone to remove the surfactant layer left behind.

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Methods to Detect Contamination

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Particulates

- Optical microscopy
  - Brightfield/darkfield
  - Nomarsky interference contrast
  - Phase contrast
- Electron microscopy
  - SEM
  - TEM
- Atomic force microscopy
- Photoluminescence
- Electroluminescence

Chemical

- Photoemission spectroscopy (UPS/XPS)
- SIMS
- Electron microscopy
  - SEM with EDX
  - TEM with spectroscopy
- Device measurement
  - C-V technique for MOS.
  - Lifetime measurements

So, that is all that I have on advanced cleans. A lot of the cutting edge cleaning details are trade secrets and not available but I have given a flavor of the general trends towards advanced cleaning. We will end this lecture with a discussion on how to detect the contamination.

We have talked about how to optimize the films, but any optimization requires a method to detect the contamination so that you can optimize the recipe. There are different techniques to detect particles and chemicals. For particles, the common ones are optical microscopy. Simple microscopy often does not work because the particles are small, but there are certain tricks that you can play, for example, often particles are better visible in darkfield images. Nomarsky interference contrast is a good way to see some of these particles as it gives you 3D depth perception that allows you to identify particles. You can also use phase-contrast optical microscopy to highlight topology.

Next, you can use SEM/TEM. The only challenge is that sometimes if the contamination is very sparse, you then to hunt for the particles which might be hard to do, but if the contamination is pretty dense then it is very easily visible in SEM/TEM. You can also use Atomic Force Microscopy (AFM), especially in cases where you do not have

conductive substrates. Photoluminescence and electroluminescence are electronic methods of measurement. The mechanism behind these is that the contamination will affect electronic properties. So, even though you are not directly measuring the particulate contamination, you can measure the effect of contamination by measuring the electronic properties which is what PL and EL do. If you are looking for chemical contamination a common technique is to do spectroscopy with UPS, XPS or SIMS. The only issue with this approach is the minimum limit of detection is pretty high ($10^{16}/cm^3$ for XPS, around 0.1 % of the surface). So, for detecting very sparse contamination UPS and SEMs are not very effective. If you can look at the contamination in an SEM you can also do an EDS to see what it is composed of, but by far the easiest way to detect chemical contamination is to look at the electronic properties. For example, capacitance-voltage and lifetime measurements are much easier and more quantitative ways of measuring chemical contamination in modern fabrication.

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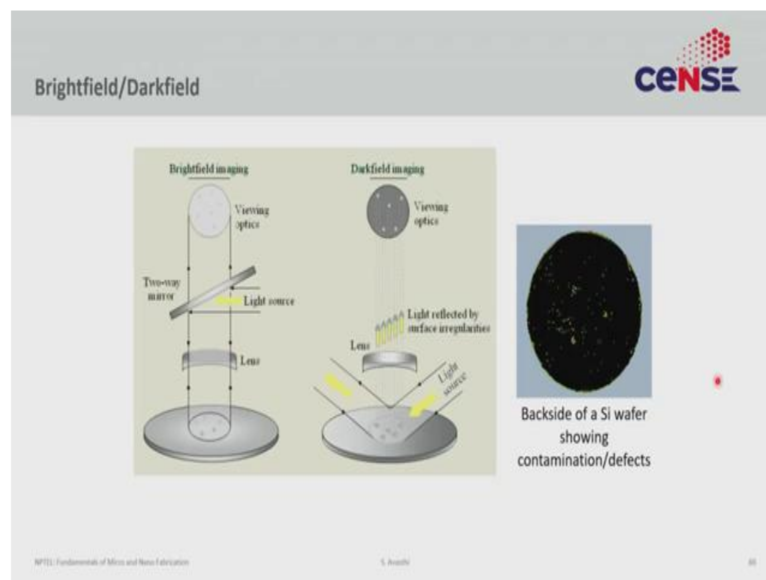

Here is an example of the backside of a wafer in the dark field. In the dark field, you look at the light that is scattered by the particles and not that is reflected by the surface. The contrast is such that the particles appear as white spots on the surface and that is much easier to see than to try to image the same particles in a brightfield image.

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SEM is another common example. Here, you see some particles on the surface that are removed after cleaning. This works as long as the particles on the surface are not very sparse but have a reasonable amount of density.

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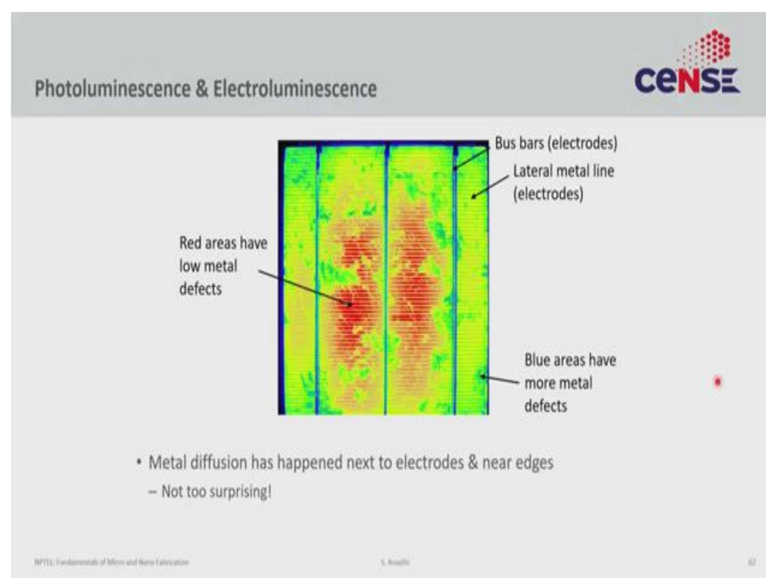

And finally, this is what PL and EL type of images look like. This is a solar cell (don't need to know how the cell or EL works). The grid-like structure you see on the top is the electrode that is just part of the structure, but more interesting is that you see different shades of color; red, green, blue. The red areas have low defects and the blue areas have

high defects. When you process a wafer, it does not come out uniform because defects can be randomly placed and that random distribution of the defects is visible in the EL image. The middle of the wafer which was probably not touched by anything is cleaner, the edges of the wafer are dirtier. If there is a systemic problem, you can look at an image and see where the systemic problem is coming from.

In these three parts, we have discussed cleaning and the bottom line is that cleaning is a very important step, and must be very carefully done. Before any critical step in microfabrication, you should consider the best way to clean your substrate because that would give you the best performance. Most failures of performance tend to be failures of keeping a close watch on purity; purity is something extremely crucial in semiconductor fabrication.

Thank you.