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Lecture - 25 Physical Vapor Deposition: Sputtering

The next chapter in our ongoing series on physical vapor deposition, under the larger module of additive processing, is sputtering.

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We have covered the basic idea of sputtering in the introductory lecture. Once again, we have plasma. You might see a theme here. Whenever we have to provide the energy, we can either do it thermally, for example, in evaporation or through other means like plasma. Sputtering is a version of physical vapor deposition, where you provide the energy electrically, not thermally.

Plasma is ionized gas. In this case, we start with argon. You could have chosen another gas, but argon is an inert and a heavy gas, so it suffices. We ionize it by applying a bias between the electrodes and form a plasma. Ar^+ ions get attracted to the cathode, accelerate, and hit the cathode surface with some momentum. The collision is hard enough to eject particles from the cathode (target) surface. If you beta a hammer on a wooden or stone surface, you see chips flying out. Sputtering is a similar process but at a microscopic level. Individual atoms or clusters eject.

These don't have any charge, so they are not unaffected by this electric field. They go from high concentration to low concentration, which usually is from target to the substrate. It is often line-of-sight and depends on the mean free path and a few other things. This process is inefficient for particle ejection, so most of the energy dissipates thermally. So, you need water cooling for the target. Otherwise, it heats up or even melts in extreme cases. There is grounding to contain the electric field lines.

Where, in your day to day life, do you interact with plasma? It is how plasma looks. It is an actual photograph of a sputtering gun, and this pink glow is due to the (argon) plasma. Ar^+ ions from the plasma bombard the metal target. Fluorescent light is a gas discharge lamp where, cathode ray ionizes and excites gases, thereby emitting light, while the positive ions bombard the cathode. Here, we deliberately design the system to maximize the cathode bombardment by the ions to sputter (eject) the material.

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The simplest and probably the oldest sputtering method is DC. The idea is that you apply a large bias that can cause the gas to break down. For sputtering, you need Ar^+ ions, but what you flow inside the chamber is uncharged or neutral argon gas. So, we need some energy source to strip out an electron from this argon atom to form Ar^+ ion. That source is typically the accelerated electrons. Where do you get the electrons? You always have some free electrons from ionization of the gas by cosmic rays or UV radiation, or emission from the cathode. They accelerate under the applied bias, interact with the

neutral Ar atoms, and ionize them to Ar^+ and extra e⁻. It starts a chain reaction where these electrons cause cascading ionizations. Above a critical size, the plasma becomes self-sustaining, where you get the required electrons from the ionization. These Ar^+ ions accelerate under the electric field and bombard the surface like ion implantation, though the energies are much lower.

These high-energy Ar^+ ions knock the target (at the cathode) and sputter some atoms out. You get the energetic electrons to sustain the plasma by accelerating them under the electric field for some distance. The mean free path (λ) limits the maximum energy that the electron or Ar^+ can attain in this electric field. If the gas is very sparse, λ is long. The charges will have a long time to accelerate and acquire kinetic energy before colliding with a gas atom/molecule. However, if λ is small, they will not.

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It is a typical sputtering chamber. You deposit the target material onto the substrate. You can place either of them at the bottom, but you need to apply a negative bias to the target and a positive to the substrate. It can be a DC bias of 1-3 kV. It can also be AC (in RF sputtering) or pulsed DC. A new sputtering system called high impulse magnetron sputtering has emerged, which we will not discuss here.

You maintain the pressure of 10-100 mbar inside the chamber. As we shall see, this range is critical for self-sustaining plasma. Ar^+ ions bombard the cathode, and the neutral ejected atoms go towards the substrate. You pump (argon) gas in through MFC to form

ions. Somewhere at the bottom, you have a pump that maintains the vacuum. You get to the base pressure around 10^{-6} mbar, but as you flow argon during the deposition, the deposition pressure is a little higher, around 10-100 mbar.

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Sputtering yield (Y) is the number of target atoms that come out for every Ar^+ ion that bombards the surface. Y=1 means, for every Ar^+ ion, one target atom comes out. Y depends on the inert gas you use. You can use helium, neon, argon, or xenon. If you use helium, you don't get a high yield because it is a light ion. It takes a lot more energy or several He⁺ ions to eject one atom from a metallic target with heavier elements. The sputtering yield increases as you go from helium to xenon. However, xenon is very expensive, and for practical reasons, is not used. For every sputtering target material, there is a threshold or minimum energy required to eject an atom, around 10-100 eV.

The sputtering yield does not just depend on the ion chosen to bombard, but also on what you sputter. Y is lower for heavy metals like Ag and higher for light materials like Al. Y depends on θ too. The flux of Ar⁺ ions coming at a higher angle can cause more sputtering. Ejection is better at oblique or glancing impingement. You get the highest yield around 60°, and not at the normal incidence. The modern sputtering systems take care of this using an elaborate system of magnets that tune the θ . You require magnets for magnetron sputtering also, which we will discuss later.

To summarize, argon is the most cost-effective option among the inert gases to get a higher sputtering yield. Heavy metals sputter slowly, and there is an angle dependence.

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Sustained Plasma vs. Deposition Rate	CENSE
Sustained Plasma	Deposition Rate
 If the distance between electrodes (L) is too small Fewer collisions between electrons and Ar → No plasma If Ar pressure (P) is too low Too few Ar atoms for electrons to collide with → No plasma 	 λ_{Alr}(in cm) = ^{6.5×10⁻³}/_{P (mbar)} at P= 50 mbar, λ=0.5 cm Source atoms collide hundreds of times before deposition
• For plasma, $L \times P > 0.6$ mbar	• Rate $\propto \frac{1}{L \times P_{e}}$
• For dense plasma, $L \times P$ should be high	+ For high deposition rate, $L \times P$ should be low

The chamber pressure and length requirements to sustain a dense plasma are at loggerheads with those for a higher deposition rate. Let us discuss how you get a sustained plasma. Consider DC sputtering with a small inter-electrode distance (L). There will be very few collisions between electrons and argon, and hence, less ionization and sparse plasma. If the Ar pressure (P) is too low, you again have the same problem. The mean free path (λ) is inversely proportional to P. Even if L is large, but if λ >L, the electrons may not collide with Ar atoms and ionize them. For sustained plasma, you need a minimum L×P. Empirically, the condition is L×P > 0.6 mbar-cm. L/ λ (or L×P) is proportional to the number of times e- collide with Ar in the inter-electrode space. For dense plasma, you need multiple e⁻-Ar collisions, and hence, L×P should be high.

However, for higher deposition rates, you want the sputtered atom to suffer as fewer collisions as possible. The mean free path of air (or the gas used) is ~0.5 cm at 50 mbar pressure. If your substrate to target distance is 10 cm, for $\lambda \sim 0.5$ cm, the atoms sputtered from the target suffer 20 collisions before arriving at the substrate. Each collision can deflect it out of the direct path and reduce its probability of reaching the target. Similar to evaporation, collisions reduce the material efficiency and lower the deposition rate.

For higher deposition rates, you want the number of source atom-Ar collisions $\sim L/\lambda$ (or L×P) to be as small as possible. For sustained plasma, you want L×P to be large. These are opposing requirements. It is one of the reasons why it is hard to get reasonable deposition rates in simple sputtering systems, as compared to evaporation.

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This graph from the book by Milton Ohring demonstrates what we just discussed. This book is a good read. You have sputtering yield and relative deposition rate on the right, and the current (proportional to the ion flux) on the left. Under typical sputtering conditions, you get this U shaped curve. At low Ar pressure, you don't have a large discharge current. You have enough sputtering yield (transport efficiency), which reduces at very high pressures. Optimum lies somewhere in the middle. For typical sputtering, you have to be around 80-140 mtorr, and the maximum deposition rate you get is 10 nm/min, which is relatively low.

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Now, this would have been the end of sputtering, except people are smart. Somebody came up with the idea of using a magnetic field to change this optimization. The charged particles go in a spiral or circular path in the magnetic field. Using that, you can make the plasma inside the chamber non-uniform by confining the electrons near the cathode. Locally, the electron concentration is enhanced (without increasing the pressure) at the expense of a lower concentration elsewhere. It improves the ionization efficiency near the target.

Look at a typical sputtering gun. In the top view, the magnetic field lines go radially outwards. In the (zoomed-in) side view, the magnetic field lines are coming out of the screen, parallel to the target. The radial magnetic field forces electrons that accelerate perpendicular to the target (under the electric field) to go in a circular path around the field line. The electron trajectory looks circular from the top. From the side, it appears as if the electron is jumping and moving around the target.

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It doesn't matter if the target is circular or rectangular. Look at the path of electrons hopping on it. On a used sputtering target, you can see these erosion lines. These represent the path where most of the electrons are confined. You get a lot of plasma there because the electrons have a high probability of colliding with and ionizing Ar to Ar^+ . Ar^+ ion then bombards the substrate to eject material. So, you get these erosion lines.

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What level of the magnetic field do you need? Does it also not affect the Ar^+ ions? The bending radius under a magnetic field satisfies this relation. At V_d around 100 V &

 $B \sim 100$ Gauss, the electron radius is 0.3 cm, so the electrons are tightly confined. The bending radius of Ar^+ is 91 cm. The curvature of their path is negligible. Practically, for a typical substrate-target distance, the Ar^+ ions essentially go straight. You choose the magnetic field intensity such that the Ar^+ ions are barely affected, but the electrons are confined. The difference between these comes from the mass. Ar^+ ions are much more massive, so it is much harder to bend them, as compared to electrons.

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This figure shows how magnetron improves sputtering. The maximum deposition rate with the non-magnetron sputtering is around 10 nm/min with ~ 100 mtorr pressure. The introduction of a magnetron allows a much higher rate (~ 1000 nm/min) at a much lower pressure (~1 mtorr). It is a significant improvement for a minimal cost. A lot of these magnets are simple neodymium magnets, which are relatively cheap and easy to install.

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RF Sputtering		Cense
 DC sputtering cannot be used for in – E.g. oxides, nitrides, etc. – Charge builds up on the cathode – Plasma extinguishes Solution is to use AC power! – At low frequency (< 100 kHz), both in – At high frequency (> 1MHz), ions car – RF sputtering usually done at 13.56 l 	nsulating materials ons and electrons react to switching voltage unot keep up. Only electrons react MHz	
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What is RF sputtering, and why is it required? We have discussed DC sputtering. It works perfectly fine for conducting targets, but for insulating targets such as silicon dioxide or aluminum oxide, it may not. That is because most of the applied voltage would fall across the thick insulator (because of its high resistance ~ $G\Omega$), and not across the plasma to do any ionization. In a sustained plasma, the bombarding Ar^+ ions neutralize at the cathode surface. Unlike conducting targets, insulating cathodes can't provide electrons to do that. All that positive charge piles up on the target surface and prevents further Ar^+ ion bombardment. Ultimately, the plasma will extinguish, and the sputtering will stop as the target charges up.

The simplest solution is to use not DC, but RF (oscillating) bias. A capacitor can't conduct DC, but it can AC. So, using RF power instead of DC, you can create plasma even on insulating targets. Often for oxides, nitrides, or any insulator, you can use RF sputtering. What frequency should we use? At very low frequencies, ~ 100 kHz, both ions and electrons respond to the oscillating voltages. At high frequency (> MHz), ions (Ar⁺) can't keep up because of inertia. Typically, you do RF sputtering at 13.5 MHz, which is in this regime. Only electrons react, while the Ar⁺ ions stop. That has significant consequences.

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Here is that consequence. In an AC bias, for half the cycle, you bombard the target with Ar^+ ions. In the other half, the bias reverses, and you now bombard the substrate. If all other things are equal, you deposit in one half of the cycle and etch in the other half. Why should there be any net deposition? There is a reason why we have selected the RF frequency > MHz. In this regime, Ar^+ ions don't react to the RF bias as they can't move that fast and accumulate in the middle. Electrons go left in one half of the cycle and right when the voltage switches in the other half. They go back and forth while the ions stay in the middle. The DC voltage across the inter-electrode space looks like this. You have applied an AC voltage; however, the difference in inertia between Ar^+ and electrons induces a DC voltage.

The net DC voltage difference between the electrodes is still 0, as you have only applied an AC bias. But somewhere in the middle of the chamber, you have a positive DC voltage. This induced steady-state DC potential depends upon the chamber design and a few other details. Even then, how do we get a net deposition?

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In half of the cycle, ions sputter the target, and in the other half, the substrate. It is because of the same voltage on both the electrodes. So, you deposit in one half of the cycle and etch in the other. If both of them are equal, you will not have a net deposition in this symmetric case. You can solve this by changing the electrode area.

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You don't keep the target area and the area of the substrate the same. The induced DC voltage depends on the electrode area. The ratio of the induced DC voltage at the electrode is inversely proportional to the 4th power of the area ratio, which is a strong

polynomial dependence. The dotted line represents the symmetric area case, while the red line represents the asymmetric area case. The area is scaled such that there is a large voltage drop at the target where you want the sputtering, and a small voltage drop at the substrate, where you want the deposition to happen. At the target, acceleration is more, so the erosion is more. The area has to be smaller, as the voltage is larger at the smaller electrode. Just by scaling it, we can create a preferential deposition. In your sputtering systems, the chuck or the sample holder will have a greater area than the sputtering gun.

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Let's look at the typical energy values. Area scaling reduces the V_{substrate}, but not completely. So, there is some Ar^+ bombardment even on the substrate. Most of it happens on the target. Ar+ ion bombardment energy on an electrode is proportional to its induced Dc voltage. In typical sputtering, V_{substrate} ~ 20 volts. You can add additional DC bias on top of this RF bias to enhance it to 100-500 V. You can use this energy to change the properties of the deposited film. This additional source of energy is like substrate temperature, which improves surface diffusion.

The neutral metal atoms ejected from the target also come with some kinetic energy $E_{neutral} \sim 2-20$ eV. Substrate bias is one handle that you can use to tune the film properties. The exact value of $E_{neutral}$ depends on the substrate to target distance and the mean free path (chamber pressure). At higher pressure, $E_{neutral}$ is low. If you get a lot of cracking in the film due to the bombardment of the neutral atoms with a high $E_{neutral}$,

increase the sputtering pressure to reduce $E_{neutral}$. If $E_{neutral}$ is not enough to form more crystallites or larger grains, perhaps you should reduce the chamber pressure. That increases $E_{neutral}$ and improves surface diffusion.

How does the $E_{neutral}$ compare what you get in evaporation? There, the energy levels were ~ 0.1 eV, while in sputtering, several eV. This order(s) of magnitude higher energy is why sputtering can give much different morphology than evaporation.

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We saw that in the films deposited by the evaporation of the alloys, it is hard to get the same stoichiometry as the source. The film stoichiometry depends on the vapor pressure ratio of the (two) metals, and not on the source stoichiometry. Sputtering does not have this problem. It is an intriguing mathematical exercise to prove that when you sputter alloys, you get the same stoichiometry in the film as in the source.

Milton Ohring's book has a detailed discussion on this, which we will not include in the curriculum. Unlike evaporation, you can have a nichrome alloy target and expect to get a nichrome film on the substrate.

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Reactive sputtering is another advantage of sputtering. The idea is to introduce a reactive gas such as oxygen or nitrogen, and that reacts with the neutral species to form/deposit compounds. For example, you can use an Al target, introduce oxygen in the chamber to deposit Al_2O_3 or sputter a titanium target, introduce ammonia or nitrogen into the deposition chamber, and deposit TiN. You can use it to deposit various types of compounds such as metal oxides, nitrides, carbides, etcetera.

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Reactive sputtering is a little more complicated than just a physical vapor deposition because it has a chemical reaction. It complicates some process parameters. For example, you may have to worry about how much oxygen to flow. If it is not enough, you may not get stoichiometric films. Here is an example of tantalum nitride deposition from a tantalum target. Depending upon the partial pressure of nitrogen inside, you get different versions of titanium nitride, with different resistivity and properties.

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Some discussion on the nucleation and growth during the sputtering would be useful. We looked at a similar diagram for evaporation, where we had three zones; zone 1, zone T, and zone 2. The difference between those three zones was the substrate temperature. In sputtering, you also have access to the pressure as a parameter, which can change the energy at which the neutral atoms bombard the surface.

The neutral species bombardment is an additional and significant source of energy. It changes the microstructure, just like the substrate temperature. Unlike evaporation, the phase diagram of a sputtering system is two dimensional. The effect of the homologous temperature is similar to what you see in evaporation. Below T/Tm = 30 %, you are in zone 1, and then transition into zone T, and if T/Tm > 0.5, in highly crystalline zone 2. The reason is as you increase the substrate temperature, you provide more energy to the adatoms for surface diffusion. It allows the incoming atoms to rearrange themselves and get into the lattice position, and give you a more crystalline film. In zone T, you have

competitive growth, where one or two orientation kinetically win over the others as the film gets thicker.

As you increase the pressure, the mean free path (λ) becomes smaller, and the atoms suffer more collisions, and hence, lose more energy. If you reduce it, the adatom energy increases. At a lower temperature, they can do what they could have done at a higher temperature. One way to think about it is as you reduce the pressure, the Zone T transition temperature reduces because the adatoms have higher energy (from the electrical power) without increasing the substrate temperature. So, the range of zone-1 reduces. Zones T and 2 starts at a lower temperature. You also have a zone 3. It is how pressure and temperature can affect the film morphology. These conditions become more complicated for reactor sputtering, but we will not discuss it in this course.

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Let's discuss the advantages and disadvantages of sputtering. The most prominent benefit is that large-size targets are possible. In evaporation, we had point sources. The crucibles or the resistances were small, so we had this substrate to target distance versus uniformity trade-off. In sputtering, you can make arbitrarily large targets, and hence, you get arbitrarily large areas for uniform deposition. However, you still have to make sure that most of the voltage drop near the target. The chuck or the substrate size must also increase, but that is often easy to do. Another advantage is better control, and more reproducible films, especially alloy deposition, which evaporation doesn't allow. You can do in-situ cleaning using plasma. In the dry cleaning method, we used plasma to clean the substrates, which we have here in-situ. You can change the direction of the electric field to clean the substrate before deposition. There are no X rays generated because there are no electron beams. You get better step coverage partly because the mean free paths are much shorter. The arrival angle of the flux is wider. So, it deposits in all directions. It's less directional than evaporation. You can control film stress using the energy of the incoming atoms, which you, in turn, control by changing the voltage.

The disadvantage is that it is a much more expensive process. The deposition rates are relatively lower than evaporation. Physical bombardment degrades soft materials. If you deposit on an organic semiconductor, sputtering creates a lot of damage; evaporation does not. You incorporate more impurities (and argon) from the gas because you function at higher pressures. Better step coverage prevents sharp profiles, which is a problem for liftoff.

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	Evaporation	Sputtering
Energy type	Thermal	Mechanical
Rate	1000 atomic layers/s	1 atomic layer/s
Impact energy	~0.1 eV	1 10 eV
Density	Low	High
Adhesion	Often low	Usually good
Substrate heating	Low	Moderate for RF. High for DC
Surface damage	Very low except X-rays from e-beam	Ion bombardment damage
In-situ cleaning	Not an option	Easily done
Vacuum	High (<10 ⁻⁶ mBar)	Low (1-100 mBar)
Directionality	Highly directional	Poorly directional
Step Coverage	Poor step coverage	Good step coverage
Purity	High	Gas atoms implanted in films
Temperature of the target	Beyond melting point	Little above room temperature
Choice of material	Limited	Almost unlimited
Stoichiometry control	Poor	Excellent
Technology	Simple	Complex
Cost	Low	High
Controllability	Low	High
Scaling up	Difficult	Easy
Uniformity	Poor	Can be very good

This table compares evaporation and sputtering. You often have to decide which one to choose. The energy type in evaporation is thermal, while it is mechanical in sputtering. The deposition rate in evaporation can be much higher than in sputtering. However, the impact energy in sputtering is a little higher, which allows you to get the same quality of films at much lower temperatures, as we discussed in the Thornton diagram. The density of films in evaporation is low. You can sputter dense films by bombarding the surface.

The adhesion can be low in evaporation, but usually good in sputtering, because of bombardment. The substrate does not heat much in evaporation, but it does in sputtering, because of the impact of Ar^+ ions, especially during RF sputtering. The surface damaged in evaporation is minimal because the impact energy is low. In-situ cleaning that you can do in sputtering is not an option without additional hardware in evaporation.

The vacuum is high in evaporation and low in sputtering, so the directionality is very high in evaporation, but not so much in sputtering. The step coverage, which is lesser in evaporation, is better in sputtering because of lesser directionality. Purity is higher in evaporation because of the higher pressures.

As you have to melt the target in the evaporation, you have a limited choice. You can't deposit the materials that are very hard to melt. Stoichiometry control is poor. However, in sputtering, the target becomes a little hot but more or less at room temperature because of water cooling. That allows you almost an infinite choice of materials. You can sputter tungsten, refractory materials, carbides, and nitrites; materials that have a very high melting point which you cannot evaporate.

The technology for evaporation is very simplistic. Even a student can maintain an evaporator. Sputtering takes a bit more work, though the controllability is better, and scaling-up is easier. It is why sputtering has won out in CMOS processing.



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Pulse laser deposition is a cousin of sputtering. It is a cross between evaporation and sputtering and has advantages of both. Here, you provide the energy by a laser beam. The laser beam is pulsed, hence the name - pulsed laser deposition. It is a very high power laser. The first few nanometers of the target absorb it. The energy is so high that the volume that absorbs the laser instantly sublimes or ablates.

It doesn't just ablate but is stripped of the electrons and ionizes. It forms a laser plume that has plasma and gases. It expands and the deposits vapors on the substrate and then extinguishes. There is no sustained plasma because it is one pulse. Then another pulse of laser comes in. With every pulse, you evaporate or ablate the top few nanometers of the target. It gives excellent stoichiometric control, which allows you to deposit films that are otherwise very hard to deposit with sputtering or evaporation.

Note that the laser is very intense. It pumps ~ J/cm^2 per pulse. For a pulse duration of 10 ns, the intensity ~ 100 MW/cm², which is a very high amount of power in a small area. Scaling-up is an issue. Commercially, very few tools can deposit uniformly over 6 inches. That is a challenge. It is still an R&D tool, not so much a commercial tool.

It ends our discussion on sputtering. Next, we shall look into the art of metallization. We know how to deposit metals through evaporation and sputtering, but you need to understand a bit more processing to make suitable contacts to devices.