Problems

P2.1 Analyze Eq. (2.2) in the context of a Thermal Etching process that is limited by the adsorption step.

Equations such as Eq. (2.2) are called an Arrhenius equation. This equation was proposed by Svante Arrhenius based on empirical observations of the temperature dependence of chemical reaction rates. The physical interpretation of this equation is quite complex and goes beyond the scope of this book.

Equation (2.2) describes an exponential temperature dependence of the chemical adsorption rate. The adsorption rate strongly increases with temperature because the negative exponent is smaller for larger temperature values. Chemisorption of neutrals is one of the elementary surface processes of many etching processes such as Thermal Etching and Thermal Isotropic ALE. Increasing the temperature will increase the rate in a Thermal Etching process if it is rate limited by chemisorption.

The temperature sensitivity of the adsorption rate increases with the activation energy, $E_{a,A}$. The activation energy depends on the kinetics of the surface reaction, which may include dissociation of a physisorbed molecule as shown in Figure 2.4. The activation energy can be minimized by selecting the appropriate reactant molecules. Fluorine, for instance, can be delivered to a surface in the form of HF, XeF_2, NF_3, SiF_4, SF_6, or other molecules. The activation energies of these gases vary for different surfaces. Therefore, the best etching gas must be identified experimentally.

The activation energy is strongly lowered when using radicals because they have free electrons and can bond to the surface directly. The activation energy is close to zero and the resulting Radical Etching process is not temperature sensitive as long as the adsorption step is rate limiting.

The actual surface processes during Thermal Etching are more complex. While Eq. (2.2) predicts that the chemisoption rate will be higher at higher temperatures, Thermal Etching rates frequently do not increase with temperature. The reason is that at higher temperatures, the adsorption rate can become limited by the physisorption rate of the precursor molecule. Physisorbed species are only weakly bonded to the surface. At higher

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temperatures, immediate desorption of the physisorbed molecules may become limiting. Therefore, an adsorption rate that decreases with temperatures can be observed in the adsorption curve for many molecule/surface combinations.

The adsorption rate is also a function of the surface coverage. If the entire surface is covered with adsorbed species, the term $(1 - \theta_A)$ as well as the adsorption rate will be zero. In a Thermal Etching process, this would be the case if the desorption of etching products is the limiting step. This illustrates that it is important to always analyze which step is rate limiting to find the right parameter to increase the etching rate.

The constant or pre-exponential factor k_0 is a constant for each chemical reaction. It can be changed to a certain degree by selecting different etching gases.

Finally, Eq. (2.2) can be used to extract the activation energy of a chemisorption reaction from experimental data. The natural logarithm of the etching rate can be plotted as a function of the temperature reciprocal. The slope gives the activation energy of the rate-limiting step, for instance chemisorption, divided by the universal gas constant.

P2.2 Calculate E_{th} for the sputtering of silicon with argon using Eq. (2.7) and the binding energy for silicon E_0 of 4.7 eV. Compare with the experimental results in Table 2.1.

Using the atomic mass for argon of 40 a.m.u. and for silicon of 28 a.m.u., the calculation gives a sputtering threshold $E_{th} = 21.6$ eV. This is quite close to the values of 20 and 27 eV given by Oehrlein and Yamamura, respectively (Yamamura and Bohdansky 1985; Oehrlein et al. 2015).

P2.3 Using Eq. (2.18), calculate the relative flux of neutrals to the bottom of a round tube with an aspect ratio of 50 for several reaction probabilities or sticking coefficients between 0 and 1. Assume a transmission probability of 0.025 29. This value can be found on p. 36 of the third edition of “A user’s guide to vacuum technology” (O’Hanlon 2003**).**

The results are given in the table below. The data shows how sensitive the neutral flux is to the sticking coefficients or reaction probabilities. Radicals are very reactive. They readily adsorb or etch the material on the sidewall. Therefore, radical etching has a typically larger ARDE compared to less reactive neutral gases. The results also illustrate why RIE of vias and trenches with aspect ratios of 10 and larger is mainly a chemical sputtering process. The reason is that neutral and radical fluxes to the bottom of the feature are negligible according to Monte Carlo simulations (Huang et al. 2019).

Sticking coefficient, S	$J_{n,b}/J_{n,t}$
0.0	1.000
0.2	0.115
0.4	0.061
0.6	0.041
0.8	0.031
1.0	0.025

P2.4 Using Eq. (2.3), calculate the change in desorption rate R_D when the activation energy $E_{a,D}$ is reduced by a factor of x ($x < 1$). Interpret the result in the context of a Thermal Etching process that is limited by the desorption of etching products.

A decrease of $E_{a,D}$ to $x * E_{a,D}$ changes the desorption rate to $y * R_D$. Dividing both sides of the two equations and solving for y gives $y = e^{(1-x)E_{a,D/RT}}$. This means that the change of the desorption rate with activation energy is still dependent on the initial value of $E_{a,D}$ and T. However, it can be unequivocally concluded that the desorption rate increases when the activation energy is reduced because $y > 1$.

We can apply this result to a hypothetical Thermal Etching process that is limited by desorption of etching products. Let us assume that the surface condition of the wafer, such as the presence of contaminants, induces a change in the activation energy. The Thermal Etching process would be less sensitive to these surface conditions at higher processing temperatures.

P2.5 A spacecraft enters the argon-rich atmosphere of a hypothetical extrasolar planet. The heat shield is made of tungsten. Is it possible that fast neutral impact initiates an etching process? Use Table 2.1 in your calculations.

The purpose of this problem is to get a feel of the velocity of sputtering ions.

Let us calculate what velocity the spacecraft must possess to initiate the argon sputtering of tungsten. Using the spacecraft as the frame of reference, this is the same velocity the argon neutrals will have when they impact the spacecraft. The kinetic energy can be calculated knowing the velocity and mass of the argon atoms and be compared with the sputtering threshold energy.

Table 2.1 shows the reported sputtering thresholds for tungsten with argon. Let us pick 20 eV. We can use $E = 1/2mv^2$ or $v = \sqrt{2E/m}$ to calculate the

velocity the argon neutrals must possess to cause sputtering. An energy of 20 eV equals $3.2E{-}18\,\mathrm{kg/(m^{-2}\ s^2)}$ and the mass of an argon atom is $6.6E{-}26$ kg. The resulting velocity is 9800 m/s. The speed of sound is 343 m/s. Hence, the spacecraft would have to travel with 28 times the speed of sound for argon neutrals to sputter the tungsten heat shield. Coincidentally, a typical reentry speed of the space shuttle was 25 times the speed of sound (https://www.grc.nasa.gov/www/BGH/hihyper.html).

In reality, the erosion processes at the surface of a space craft entering the atmosphere are much more complicated. Just to name a few, different masses of the constituents in the atmosphere will lead to different sputtering thresholds. Chemically reactive species may react with the surface and lower the sputtering threshold (chemically assisted sputtering). When the temperature of the surface rises, reactive species may cause Thermal Etching, for instance, burning of carbon-containing materials. As the atmosphere becomes denser, thermal plasmas form and lead to ion acceleration beyond the kinetic energy. Beyond that, the gas flow is no longer molecular and yet different effects dominate.

P3.1 Explain why the process window of Thermal Etching is typically small. Why is this a fortunate situation for our daily life?

The reason why the process window for Thermal Etching is typically smaller than for etching with ions is that for Thermal Etching to occur, chemisorption, surface reaction, and desorption must have meaningful rates at one given temperature. The process window for Thermal Etching is the temperature interval within which etching happens. For etching with ions, higher ion energies lead to faster etching. For Thermal Etching, however, a higher energy (higher temperature) does not always increase the etching rate. Here, an upper limit for the process window exists because physisorption is suppressed at higher temperatures. Chemical reactions can also slow down at higher temperatures for thermodynamic reasons.

Thermal Etching is rarely observed in daily life because the temperatures are generally too low to stimulate surface reactions and desorption. In addition, most metal surfaces we encounter are actually covered in the thin layer of metal oxides with very high boiling points.

P3.2 Assume that a given Thermal Etching process is desorption limited. The highest etching rate on the wafer is 10% higher than the lowest due to gas flow nonuniformities. Use Eq. (2.3) to calculate the temperature delta across the wafer that is needed to compensate the flow uniformity. Assume that the base temperature is 250 °C and the activation energy 1.2 eV.

Equation (2.3) can only be used if the etching process is desorption limited. The base temperature of 250 °C or 523 K gives an etching rate proportional to R_D. Increasing the temperature to a higher temperature T gives an etching rate of 1.1 R_D.

Dividing the two equations and applying the natural logarithm gives

$$\ln 1.1 = -E_{a,D} \frac{(T - 523)}{523 * RT}$$

Because the activation energy $E_{a,\,D}$ is given in electron volts, the calculations are conducted for one molecule and instead of the universal gas constant, we use the Boltzmann constant ($k_B = 8.6E{-}5$ eV/K). Alternatively, the gas constant $R = 8.3$ J/mol K and the activation energy $E_{a,\,D} = 115.8$ kJ/mol can be used. Solving the equation for T results in $T = 524.9$ K. This means that a temperature adjustment of about 2° is sufficient to compensate a 10% etching rate nonuniformity. The temperature adjustment must be larger for processes with smaller activation energies.

P3.3 Why is the repeatability for Thermal Etching of SiO_2 with HF improved when alcohols are added and the temperature is increased?

According to Eq. (3.1), one of the reaction products of SiO_2 with HF is water, which participates in the reaction. The formation of sufficient water coverage has an incubation time and is not repeatable. Water also accumulates at the surface and the second reaction product, SiF_4, dissolves in it forming fluosilicic acid, H_2SiF_6. This process can slow down the etching rate. Running the process at elevated temperatures where water is not physisorbed helps to improve repeatability. Under these conditions, the role of water is to provide hydrogen to form a hydrogen-terminated surface that HF can react with. Alcohols can be used for the same purpose without the risk of forming a surface with physisorbed water.

P3.4 Why are halogens used in Thermal Etching?

Halogens meet the requirements for an etching reactant perfectly. They form very strong bonds with the surface, which weakens the bonds to the layers below the surface. This allows in many cases the desorption of the reaction products at accessible temperatures. The fundamental reason for this behavior is that halogens need just one electron to complete their outer shell.

P3.5 Why do chelating reactants etch metal oxides but not metals?

The reason can be found in the fact that metals form metallic bonds where the electrons are distributed across many atoms. Only very reactive species such as oxygen and halogens can interact with these electrons and form ionic bonds. Chelating reactants can then interact with the metal ions to form a chelate complex. By themselves, most chelating reactants are not able to react directly with pure metals.

P3.6 What does ΔG^0 say about the etching rate of a Thermal Etching process?

ΔG^0 depends only on the difference in free energy between the reactants and the reaction products. It must be negative for the reaction to proceed. However, ΔG^0 does not tell us anything about the rate of a reaction because it is independent of the path of the chemical reaction. The activation energy takes the path into consideration and is an important parameter in calculating the reaction rate.

P4.1 What is the role of the second surface reaction in Thermal Isotropic ALE?
The role of the second surface reaction in Thermal Isotropic ALE is to form volatile reaction species in a reaction only with the modified layer, but not the bulk material. It enables Thermal Isotropic ALE at constant temperature.

P4.2 Name three important tests that are used to identify ALE processes.
These tests are the measurement of the saturation curves, the synergy test, and the energy scan. In the case of Thermal Isotropic ALE, the energy scan measures EPC as a function of wafer temperature and in the case of Directional ALE, as a function of ion energy.

P4.3 Explain the role of etching selectivity for the design of Thermal Isotropic ALE processes with reaction-assisted desorption.
Selectivity is important in the removal step. Generally, the reactant in the removal step must etch the modified layer with infinite selectivity to the bulk material for the step to be saturated and the synergy to be 100%. There are exceptions to this rule. In some ALE processes, the instantaneous removal rate during the removal step diminishes before the entire modified layer is removed, for instance due to reactant instability and surface "poisoning."

P4.4 Why is the isotropy of Al_2O_3 ALE with HF/Sn(acac)$_2$ less than 100%?
This ALE process has been shown to leave SnF(acac) at the surface after the reaction with Sn(acac)$_2$. While HF in the modification step removes these site-blocking species on planar surface, it may not completely remove them in areas out of the line of sight. This impacts isotropy of the process negatively.

P4.5 How are conversion and ligand exchange ALE related?
In the example for conversion ALE of SiO_2 with TMA/HF, the reaction of SiO_2 with TMA leads to an exchange of cations. Silicon is replaced by aluminum. The resulting Al_2O_3 undergoes an anion exchange in the reaction with HF forming AlF_3, which is removed in a ligand exchange reaction with TMA. Thus, ligand exchange is part of this particular Conversion ALE process. The TMA also initiates the next conversion reaction with the SiO_2 underlayer. Both conversion and ligand exchange reactions proceed

simultaneously. This case must not be generalized. Not all conversion ALE processes involve a ligand exchange reaction. It is also conceivable that the conversion step is followed by a fluorination step with volatile products as in the case of WO_3 ALE with BCl_3/HF. Yet, other implementations are also conceivable.

P4.6 How does the selectivity to SiO_2 for Al_2O_3 HF/TMA change as a function of pressure?

The selectivity of the ligand exchange Al_2O_3 ALE with HF/TMA diminishes with pressure. For higher pressures, the same process cycles will result in Conversion ALE of SiO_2.

P4.7 In which step does etching occur on Conversion ALE of WO_3 with BCl_3/HF? What are the saturation mechanisms in each step?

Part of the etching of WO_3 happens in the BCl_3 step, which forms volatile WO_xCl_y products. Some of the oxygen however remains at the surface in the form of B_2O_3. It gets removed in the HF step via the formation of BF_3. So, the correct answer is that the etching occurs in both steps.

The conversion depth is self-limited, most likely due to slowing boron diffusion into the film and W diffusion toward the surface as a function of conversion thickness according to the DG model. HF cannot spontaneously etch WO_3. For this reason, the HF step is also self-limited.

P4.8 What are the saturation mechanisms of oxidation/fluorination ALE of TiN with O_3/HF?

The modification step is saturated due to slowing down of oxygen as the thickness of the oxide layer increases according to the DG model. The HF step is self-limited because HF etches TiO_2 but not TiN.

P4.9 What are the contributing factors to the throughput of Thermal Isotropic ALE processes?

The contributing factors are the depth of modification, the percentage of the modified layer that is removed in the removal step, and the cycle time. The first two factors are given by the chemistry of the reactions as well as by process conditions such as temperature and pressure. Cycle time is a function of the reactor design, for instance how quickly the gases can be exchanged.

P4.10 Explain the relationship of uniformity and throughput for Thermal Isotropic ALE.

An important factor for uniformity and throughput is whether the reactions are allowed to reach saturation. Partially saturated ALE can have a much higher throughput but metrics such as uniformity across the wafer, ARDE, and smoothness maybe impacted by partially saturated ALE. Uniformity in performance can be recovered by tuning the knobs for gas flow and temperature.

P5.1 Why is the process window for Radical Etching generally larger than for Thermal Etching?
Radicals can chemisorb directly without intermediate physisorption because they do not have to overcome an activation barrier. This makes Radical Etching generally less temperature sensitive compared to Thermal Etching.

P5.2 Why is the intrinsic selectivity for Radical Etching generally lower than for Thermal Etching?
One of the possible mechanisms to achieve selectivity is to utilize differences in the adsorption process. A given molecule may adsorb on one surface but not on the other. Because radicals have free electrons, they can adsorb more easily and are less discriminating or selective with respect to different surfaces. An example is etching of TiN and TiO_2. HF etches under the right conditions the latter but not the former. This behavior enables Oxidation/Fluorination ALE of TiN with ozone and HF. Free fluorine however etches both materials. While it is not known whether the selectivity for HF is caused by differences in the adsorption or the chemical reaction, this system is a good example for Thermal Etching being more selective than Radical Etching.

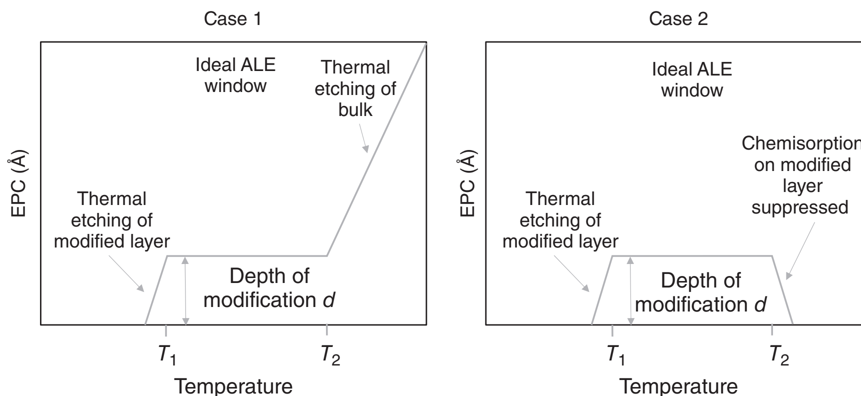
P5.3 Using Eq. (2.18), explain why ARDE for Radical Etching is generally worse than for Thermal Etching?
According to Eq. (2.18), ARDE of neutral species, such as molecules, atoms, and radicals, is very sensitive to the sticking coefficient at the surface. Because radicals have free electrons and they do not have to overcome an activation barrier, they can adsorb readily to the surface on a feature sidewall.

P6.1 Use the information in Table 2.1 to discuss why it impossible to realize a directional ALE process for silicon by forming a silicon oxide surface layer and sputtering with noble gas ions. How is this different for the same approach when applied to carbon?
During oxidation of silicon, a silicon oxide layer is formed by diffusion of oxygen and reaction with silicon. The binding energy of this layer is between 30 and 65 eV according to Table 2.1. This is higher than the binding energy of the bulk silicon with 20–27 eV. The sputtering threshold for silicon oxide is therefore higher than for silicon (Eq. (2.7)) and sputtering of silicon oxide selectively to silicon is not possible. In the case of carbon, the products of the complete oxidation reaction are CO and CO_2, which exist under normal conditions as gases. Under the right conditions during ALE, they remain adsorbed on the surface and are easily removed by ion bombardment. The relatively high binding energy of carbon with 34 eV helps achieve high synergy.

P6.2 Apply the ideal ALE window concept to Directional ALE with directional modification by ion implantation and removal with neutrals and radicals. Consider both steps in the design of the window.

The ideal ALE window is designed for the step in which removal occurs. In this case, it is the removal by neutrals or radicals. Therefore, the *x*-axis of the ALE window is temperature, not ion energy as in the case of Directional ALE with removal by ion bombardment. The removal rate can be limited by adsorption, chemical reactions at the surface, and desorption.

Regardless of the nature of the limiting step, the removal of the modified material must occur at lower temperatures than the bulk material. The lower limit of the window is the lowest temperature at which Thermal Etching of the modified layer but not the bulk material is possible. The EPC equals ideally the thickness of the modified layer. What happens as the surface temperature is increased depends on the limiting step of Thermal Etching of the bulk material. If it is desorption limited, the bulk material will start to etch at higher temperatures and the EPC increases. If the step is chemisorption limited, the bulk material will not etch because the chemisorption rate generally decreases with temperature (see Figure 3.1). In this case, Thermal Etching of the modified layer will become limited by chemisorption and the EPC will go to zero. The figure below illustrates these considerations in a highly idealized schematic:



P6.3 Explain the relationship between Thermal Isotropic ALE with Ligand Exchange and Directional ALE with surface modification by adsorption and diffusion.

For both ALE processes, the modification step can be very similar. In many known embodiments of both ALE processes, halogens are adsorbed onto the surface. They form strong bonds and weaken the bonds to the underlayers. The weakened bonds are broken in a subsequent removal step – in the case of Directional ALE by ions and in the case of Thermal Isotropic ALE by chemical reactants.

P6.4 What is the fundamental reason for the plateau in the ideal ALE window for Directional ALE?

The ideal ALE window shows the ion energy dependence of EPC. The plateau reflects the fact that EPC is limited by the depth of modification if the modified layer is completely sputtered at energies above the sputtering threshold of the modified layer but below the sputtering threshold of the bulk material. The existence of a plateau indicates perfect or at least very high synergy of the ALE process. The modification step must be long enough for the complete removal of the modified layer. In reality, nonideal processes and lack of synergy distort the ideal ALE curve and, in many cases, only a change in slope can be seen.

P6.5 Use Eq. (2.8) to explain why there is synergy for Directional ALE for energies above the sputtering threshold of the bulk material. Discuss the dependence of synergy on step time and ion energy under these conditions.

Equation (2.8) gives the relationship of the sputtering yield with the binding energy of solid materials. It shows that a modified material with lower binding energy sputters with higher yield than the bulk material. In reality, the change in molecular mass and preferential sputtering of the elements in the modified layer must be considered. Qualitatively, this statement is however true. This means that for energies above the sputtering threshold of the modified and bulk material, the sputtering rate will slow down as soon as the interface is reached. Careful selection of the removal step time can maximize the synergy of such a high ion energy Directional ALE process. The benefit of this approach is higher throughput and the ability to etch features with high aspect ratios.

P6.6 What is the mechanism that enables Directional ALE to improve surface smoothness in many cases?

While not all of the mechanisms are understood, one reason is high ion mobility of surface atoms under ion bombardment below the sputtering threshold of the bulk material. This mechanism seems to be at play for Directional ALE of silicon and metals. Other mechanism that may contribute to the smoothening effect are a higher reactivity of convex surfaces in the modification step, higher sputtering yields at oblique surfaces, and sputtering redeposition from surface peaks to valleys.

P7.1 Explain the similarities and differences between chemical and chemically assisted sputtering.

Chemically assisted sputtering is based on the synergy between neutrals and ions. The neutrals are the source of the chemical components that weaken the surface bonds. Ions provide kinetic energy to remove the material from the surface. This mechanism implies that the ions are mostly chemically inert, for instance noble gas ions. Chemically assisted sputtering is the main mechanism for Directional ALE and is very important for RIE of features with low aspect ratios.

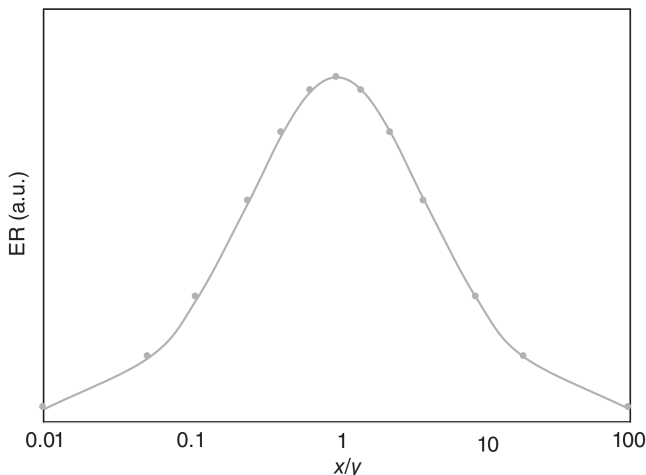
In chemical sputtering, the ions are the source of kinetic energy and chemically active species. For instance, bombardment of silicon oxide with CF_3^+ ions causes chemical sputtering at high enough ion energies. This mechanism is deemed to be the main path for etching of silicon oxide holes with aspect ratios above 10 : 1.
It is very important to distinguish between these two sputtering mechanisms because their ARDE behavior is very different.

P7.2 Explain the root causes for ARDE for hypothetical pure chemical and chemically assisted sputtering etching processes.
ARDE for pure chemical sputtering is caused by the attenuation of the ion flux. Attenuation is caused by the finite angular distribution of the ions. Assuming that the reaction products are volatile and do not redeposit, this is conceptually the only mechanism for ARDE.
ARDE for chemically assisted sputtering is caused by the attenuation of both neutral and ion fluxes. Because neutral fluxes are not directional, they will attenuate much fast than the ion fluxes and ARDE is more severe compared to chemical sputtering.

P7.3 Using Eq. (7.4), calculate a normalized etching rate as a function of the ratio between ion and neutral flux and discuss process sensitivity. What are the implications for ARDE?
Let us simplify Eq. (7.4) by substituting the ion component $x = vE_iJ_i$ and the neutral component $y = v_nsJ_n$:

$$\text{ER} = \frac{x * y}{x + y}$$

This representation shows that the etching rate is symmetric with respect to the ion and neutral components. We can plot ER as a function of the ratio x/y with the additional condition that the sum of x and y is constant. This represents a case where just the ratio of neutrals and ions is changed but not the total flux. With x/y on a logarithmic scale, the symmetry becomes obvious:



The graph shows that the RIE process is least sensitive to the ratio of ions to neutrals when operating in a balanced mode ($x \sim y$), in ion-limited ($x \gg y$) mode, or neutrals-limited ($x \ll y$) modes. One of the root causes for ARDE in RIE is the change in ion to neutral ratios. Processes where features with different CDs are etched are often designed to operate in an ion-limited mode to reduce ARDE.

P7.4 Does Eq. (7.4) contain contributions from pure neutral or radical etching?

Equation (7.4) ignores contributions from neutral and radical etching. While neutral fluxes are represented, they require ion bombardment to etch. This is called ion–neutral synergy.

P7.5 Explain the similarities and differences between Directional ALE with a Cl_2/Ar^+ process and RIE with bias pulsing using a mixed Cl_2/Ar chemistry.

In both cases, the main etching mechanism is chemically assisted sputtering assuming that radical etching by chlorine radicals can be ignored. In the case of Directional ALE, chlorine molecules or radicals adsorb onto the surface to form a modified layer. This layer is removed by chemically inert argon ions in the subsequent step.

In the case of a pulsed Cl_2/Ar plasma, the surface is modified by chlorine molecules and radicals in the bias-off phase. When the bias is turned on, chlorine and argon ions remove the modified layer. Because chlorine ions are chemically active, they also cause chemical sputtering and hence the removal step is not saturated. The effect depends on the flux of positive chlorine ions. The fact that the flux of chlorine molecules and radicals continues during the bias-on phase is another reason for the lack of saturation during removal. The surface can be somewhat depleted of the modified layer if the ion flux is much higher than the combined neutral flux. This can be achieved by using gas mixtures rich in argon.

P7.6 Using Figures 7.3 and 7.4, discuss profile implications of the angular distribution dependence of chemical sputtering.

Generally, the chemical sputtering yield is highest for vertical or normal impact. This aids in directional etching. Neutral (for instance argon) sputtering of light elements such as silicon is characterized by a peak at larger impact angles between 60° and 80° (see data for argon in Figure 7.4). This leads to enhanced sputtering of feature sidewalls and profile bowing.

P7.7 What is the implication of the formation of a mixed layer on intrinsic selectivity of RIE?

The formation of a mixed layer in RIE lowers intrinsic selectivity. It is the result of high-energy ion bombardment by reactive ions and simultaneous fluxes of ions and neutrals. The root cause is excess energy,

which overburdens more subtle chemical effects that enhance intrinsic selectivity.

P7.8 Using Eq. (2.2), explain why temperature is an effective knob to compensate ERNU caused by neutral flux nonuniformities in RIE reactors.

Equation (2.2) shows that the adsorption process is temperature sensitive. The main etching mechanism of RIE is chemically assisted sputtering and the etching process relies on ion–neutral synergy. The adsorption of neutrals can be influenced by changing the wafer temperature. This in turn changes the ion–neutral synergy and etching rate. If the etching rate is limited by the presence of passivating species, higher temperatures can suppress their adsorption on the surface, which increases the etching rate.

Temperature is also a very powerful knob to control RIE profiles. This is accomplished by changing the adsorption or sticking of passivating species on the sidewall.

P7.9 Explain the relationship between sidewall passivation etching resistance and CD microloading.

The higher the etching resistance of a sidewall passivation layer, the thinner it can be while still providing protection from isotropic etching. This is true for dense and isolated features. CD microloading is proportional to the passivation thickness differences between dense and isolated features. Hence a more etch-resistant and thinner passivation results in reduced CD microloading.

P7.10 Why is sidewall scattering a critical mechanism for RIE of high aspect ratio features?

The ions that are accelerated in the sheath of the plasma have a certain angular distribution. This means that some of the ions will impact the sidewall of a high aspect ratio feature. If the impact angle is large enough with respect to the surface normal, the ions will not sputter but scatter. This leads to greatly reduced ion energy and a larger angle than the original angle with respect to the wafer normal. Scattered ions are therefore very likely to impact the opposite sidewall and cause sputtering if their energy is large enough. This can cause lateral etching and profile bowing. A mechanism that is sometimes put forward where ions undergo multiple near specular sidewall collisions and get focused can be ruled out. In conclusion, ion scattering is an important mechanism that must be taken into consideration in the profile evolution modeling.

P8.1 Why is it necessary to tune the ion impact angle in an IBE tool? Why is it possible in IBE but not in RIE?

IBE is a physical sputtering process and has a few process parameters. The profile of a sputtered feature depends on the ion energy and impact

angle. For an impact angle normal to the wafer surface, tapered profiles are obtained due to the impact angle dependence of the sputtering yield. To obtain vertical profiles, the impact angle must therefore be larger than 0° or nonnormal to the surface. This can be achieved by tilting that wafer with respect to the ion beam.
Tilting of the wafer with respect to the source has no effect in RIE because ions are accelerated through the sheath, which would rotate with the wafer. In ion beam machines, the sheath is separated from the wafer and the ions are accelerated via ion optics.

P8.2 **Why does surface oxidation decrease the sputtering rate of some metals? Using Eq. (2.8), explain the condition for this approach to work?**
Etching selectivities are generally low in IBE due to large excess energy and the absence of chemical effects. Selectivities are governed by Eq. (2.8), which describes the effect of the binding energy on sputtering yield. It is possible to increase selectivity for some metals by adding oxygen neutrals to the process. This approach works if one of the metals forms preferentially an oxide with higher binding energy and lower sputtering yield than the non-oxidized metal.

P8.3 **Why do IBE tools operate at very low pressures?**
IBE tools operate at pressures that are several orders lower than RIE. After extraction from the source, ions travel several tens of centimeters until they impact the wafer. The pressure must be low enough to avoid gas phase collisions that would reduce the ion flux and widen the angular distribution.

P9.1 **Using Table 9.1, discuss the relationship between the temperatures of the neutral gas, the electrons, and the wafer surface at the ion impact site.**
Typical electron energies in low-temperature plasmas used in semiconductor manufacturing are in the order of 1–10 eV. This is in the range of the energies needed to ionize and dissociate neutrals in the plasma.
The temperature of the neutral species in the plasma is much lower, around 300–2000 K, or 0.03–0.15 eV per atom. This is why these plasmas are also called low-temperature plasmas. The reason why the neutral temperatures are lower than the electron temperature is that the electrons are lost to the wall faster than they are able to transfer via collisions with neutrals the energy they receive from an external energy source.
The temperature of the wafer surface at an ion impact site is much higher than the electron temperature with values around 10 to several 1000 eV. If the energy of the impinging ion is 100 eV and the collision cascade is comprised of $N = 10$ atoms, the temperature of this ensemble of atoms is over 77 000 K according to Eq. (7.7). Because the ion impact sites do not overlap under typical RIE processing conditions, the average wafer temperature

remains near room temperature. The wafer must still be cooled to avoid temperature drift toward higher values, especially for processes with high source power (ion flux) and high bias power (ion energy).

P9.2 Using Eq. (9.7), explain the significance of the electron temperature for the ion energy in non-biased plasmas (for instance, source-only TCP/ICP plasmas). How does this change when the wafer is biased by RF power?

Equation (9.7) links the sheath voltage or self-bias and the electron temperature in an unbiased plasma. The higher the electron temperatures, the higher the sheath voltage and hence the ion energy. Typical self-bias values are very low, normally around 10 eV. Most applications use bias power to increase the ion energy to values that are needed for etching, and the electron temperatures are irrelevant. In some applications, however, near 0 eV ion energy is needed. In these cases, reactors with lower electron temperatures are needed. Larger gaps and higher gas pressures are methods to lower the electron temperatures at the wafer surface.

P9.3 Why are low frequencies used to accelerate ions and high frequencies to create plasma densities in CCP reactors?

Lower frequencies produce higher sheath voltages and hence higher ion energies according to Eqs. (9.9) and (9.10). In addition, for frequencies below 1 MHz, the transient time of the ions through the sheath is shorter than the inverse of the RF frequency. Under such conditions, the ions can obtain an energy corresponding to the maximum instantaneous sheath voltage.

The plasma density increases with RF frequency in CCP reactors because the power that is absorbed by the plasma increases with the square of the driving frequency. This is deemed to be the result of an enhancement of collisional heating in the bulk plasma.

P9.4 Why does the anode to cathode ratio in CCP reactors impact the ion energy?

The reason why the anode to cathode area ratio of a CCP reactor impacts the ion energy is that the sheath voltage is proportional to the capacitance of these electrodes, which in turn is proportional to their area.

P9.5 What effects contribute to the wide, continuous IEDs in plasma etch reactors?

Several effects contribute to the wide, continuous IEDs, which are observed in typical plasma etch reactors. The width can be caused by the use of low frequencies below 1 MHz to accelerate the ions. Under these conditions, the transient time of the ions is shorter than the characteristic time of the RF signal. Depending on the point in time when the ions enter the sheath, the ions see different acceleration voltages.

The other reason why typical IEDs have many peaks and appear almost continuous can be the presence of many ionic species with different masses and sheath collisions. The latter can be avoided by lowering the pressure.

P9.6 Why are TCP/ICP reactors efficient in generating high-density plasmas?
In TCP/ICP reactors, a magnetic field is generated by a coil that is situated on top or on the sides of a ceramic window. It generates an RF electric field inside the reactor, which transfers energy to the charged species in the plasma efficiently.

P9.7 Why are the IEDs for TWB mass independent?
When the positive voltage spike in a TWB is sufficiently short, the average sheath potential is close to the quasi-DC sheath potential during the negative voltage portion of the cycle. This results in a near monoenergetic IED.

P9.8 What are the differences of the surface processes for combining single-level TWB with dual-level bias pulsing vs a combination of dual-level TWB and single-level bias pulsing?
The combination of single-level TWB with dual-level bias pulsing generates alternating near monoenergetic ions on a time scale of milliseconds. It allows implementing cyclic processes akin to multi-step ALE and MMP. Dual-level TWB and single-level bias pulsing give pulses of quasi-simultaneous ion fluxes with two well-defined energies.

P10.1 What are the mechanisms of how electrons can assist etching?
Known mechanisms of electron-assisted etching include electron-assisted desorption, electron-assisted dissociation of adsorbed molecules, surface heating, stimulation of chemical reaction at the surface, and creation of reactive radicals by electron impact dissociation in the gas phase.

P10.2 What are the mechanisms of how photons can assist etching?
Known mechanisms of photon-assisted etching include photoelectric effects in semiconductors, photon-induced chemical reaction and desorption, gas phase generation of radicals, surface heating, and the generation of surface defects by photons, which can enhance etching.

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