

TOPICAL REVIEW

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Topical Review

Physical and chemical effects in directional atomic layer etching

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**Abstract**

Atomic layer etching (ALE) has received much attention in recent years as a viable state-of-the-art patterning technique for the fabrication of future generations of nanoelectronics. Thermal excitation or plasma activation, coupled with chemical reactions have been shown as different approaches to enable ALE. In this review, the importance of surface oxidation state is considered as a viable parameter to tailor the chemical contrast that is needed in realizing ALE. With the help of thermodynamic assessment of viable reaction pathways, an alternative approach that combines both plasma and thermal ALE concepts is proposed: the physical effect from energetic ions results in not only chemical conversion but also directionality, while the chemical effect dictates the selective removal of the converted material. This hybrid plasma-thermal ALE approach allows for a simultaneous control of selectivity and anisotropy and a wider ALE window. This approach is tested on a number of model systems and could be extended to more complex materials systems that are needed in future integrated circuits.

Keywords: atomic layer etching, selectivity, anisotropy

(Some figures may appear in colour only in the online journal)

1. Introduction

The rapid emergence and adoption of new and functionally improved materials impose significant engineering challenges on device patterning at the sub-nanometer scale. In the past few decades, etching techniques have evolved from wet etch to plasma etch to enable better control of pattern transfer via improving etch rate control, selectivity, and anisotropy. Nanometer-level control of patterning, which is required for future generation electronics, imposes extremely stringent requirements on plasma exposure conditions such as time, power and bias, making the conventional reactive ion etch (RIE) process no longer precise enough due to the linear relationship between exposure time and amount of material removed. To address these issues, atomic layer etch (ALE) is

merging as a viable alternative in patterning sub-nanometer features by implementing self-limiting half-reaction cycles that guarantee the precise removal of materials [1–5]. The independent nature of two half-cycles ensures greater control of the overall etch rate compared to conventional RIE, shown in figure 1. This unique etching characteristic opens up new possibilities to realize layer-by-layer removal for novel materials, meeting patterning requirements such as extreme high aspect ratios and sharp interfaces, which are essential for nanoscale-electronics in the future. A considerable amount of effort has been invested in developing etching chemistries for a range of materials and etch rate on the order of angstrom/cycle are frequently reported [6–10]. Building upon these successes, it is logical to inquire if there exists a more general approach that can be used to develop directional atomic layer

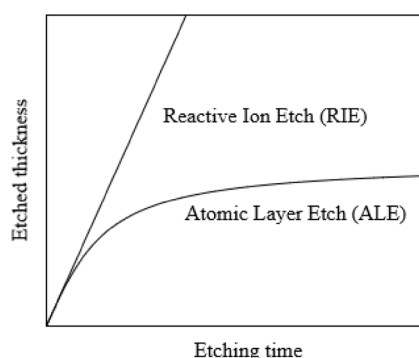


Figure 1. The self-limiting nature in ALE grants a greater control over the continuous removal of materials in RIE.

etching processes for an even broader selection of material systems, some might be on the horizon to enable more capable devices in the future.

The goal of this review is to summarize the current state of atomic layer etching, in light of available experimental and computational works, discuss persistent difficulties and uncertainties that hinder further development in this field, and suggest a broader approach capable of addressing the increasing challenges in patterning sub-nanoscale features that contain novel and etch-resistant materials.

2. The need for highly uniform atomic layer processing, especially for metals

Challenge in current and future integrate circuit processing comes as a combined effect of two major trends: an ever-increasing wafer size (300mm, to potentially 450mm), and an ever-decreasing feature dimension [11]. To reproduce sub-nanometer-sized feature with high fidelity on decimeter-sized wafers, uniformity is the key to the overall process quality and could greatly hinder the throughput if not controlled precisely. The need for more complex topographies in next-generation logic and memory devices imposes even more stringent requirements on processing uniformity and consistency. To realize high uniformity across the wafer, kinetically limited processes, instead of transport limited processes, need to be developed and implemented. A fine example of achieving wafer-scale uniformity control via a kinetically controlled process is the application of thermal atomic layer deposition (ALD), in which the reaction self-terminates as available surface site reacts to reach coverage saturation [12–15]. Conformal film coverage of complex multilayers could be achieved with little or no dependencies on processing time and surface topography. While ideal for deposition, where conformality is preferred, its etching counterpart does not benefit from this omnidirectionality. Thermally activated etching processes intrinsically lacks directionality, one of the most important requirements for etching high aspect-ratio features in making integrated circuits. The comparison between these two thermally activated processes is illustrated in figure 2.

The semiconductor industry has been actively searching for means to remove materials on the atomic level since the birth of integrated circuits. It is therefore not surprising to observe

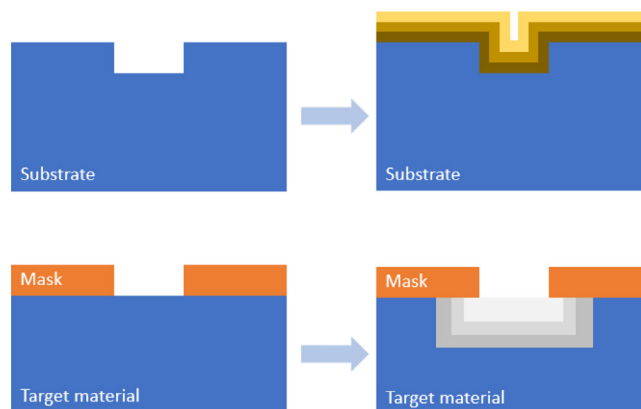


Figure 2. Illustration of thermally activated atomic layer processes: conformal coverage of ALD (top) and isotropic undercutting of ALE (bottom), where the reaction cycles are indicated by color gradients.

Table 1. Selected ALE reported on semiconductors, including elemental Si, Ge and various compounds.

Semi-conductors	Modification	Removal	Activation	Ref
Si	Cl ₂	Ar	Plasma	[18]
Ge	Cl ₂	Ar	Plasma	[19]
GaAs	Cl ₂	Ar	Plasma	[20]
InP	Cl ₂	Ne	Plasma	[10]
GaN	Cl ₂	Ar	Plasma	[21]
	XeF ₂	BCl ₃	Thermal	[16]
InGaAs	Cl ₂	Ar	Plasma	[22]
	HF-pyridine	AlCl(CH ₃) ₂	Thermal	[17]
AlGaIn	Cl ₂	Ar	Plasma	[9]

that semiconductor is the most extensively studied category of materials for ALE. As shown in table 1, ALE of semiconductors have been performed predominantly by plasma-based halogenation-ion bombardment reactions, although recent advancements showed that thermal-based halogenation-ligand exchange processes are also viable [16, 17].

As the scope of the material of interest broadens, more results on ALE of oxides [7, 23–25] and nitrides [6, 8] have been reported. The most drastic increase in the material choices in recent years of making integrated circuits is, however, in the area of metals (elemental, doped and alloyed). Metals offer superior physical properties such as high electrical and thermal conductivities—traits desirable for microelectronics integration. Additionally, the manipulation of magnetism enables many novel applications due to the growing interests in the area of spintronics and magnetic memory devices [26–29], where the non-volatile nature of changing magnetization orientation can be used to significantly reduce the power requirement. However, in sharp contrast to the rapid increase in application needs, metal patterning on the sub-micron scale remains largely unsolved, as many of these metals are etch-resistant. While controllable etching processes have been reported for a handful of metals [7, 30, 31], a systematic understanding of the underlying reaction pathways is still lacking. It is therefore the aim of this review to recapitulate reaction mechanisms from a couple different perspectives

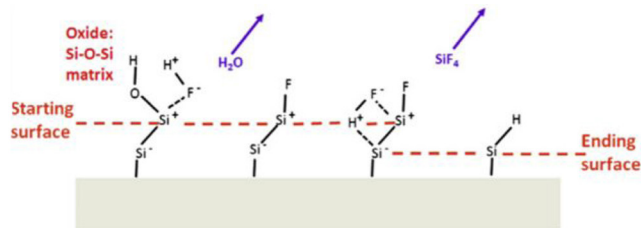
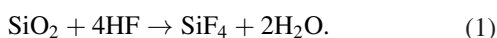


Figure 3. Mechanism leading to the formation of H-terminated Si surface by HF etching: The last step of oxygen removal involves HF attack of the Si–O bond, terminating the surface Si atom with F. Further attack of the polarized $\text{Si}^{\delta-}\text{--}\text{Si}^{\delta+}$ leads to H-termination. Reprinted from [35], Copyright 2012, with permission from Elsevier.

to develop a generalizable approach to tackle the challenges of ALE of etch-resistant metals, starting with leveraging the insight from the etching selectivity between Si and SiO_2 .

3. What can be learned from etching selectivity between Si and SiO_2 ?

It is well known that very large chemical selectivity can be achieved between Si and SiO_2 : the most effective chemistry in selective etching of SiO_2 over Si is by hydrofluoric acids (HF). Diluted HF (6:1 = $\text{H}_2\text{O}:\text{HF}$ by volume) can etch thermally grown SiO_2 at a rate of $1200 \text{ \AA min}^{-1}$, whereas the highest etch rate of Si in HF solutions is reported to be $\sim 0.2 \text{ \AA min}^{-1}$, yielding a selectivity of ~ 6000 . The overall reaction for HF etching SiO_2 could be represented by reaction (1) [32]:



At the molecular level, which is relevant to ALE, it is the effect of oxidation state and the electron configurations of the surface atom that dictate the chemically selective reactions. In the case of Si/ SiO_2 system being etched by HF, as shown in figure 3, a high selectivity is realized by the difference in electron configurations between the polarized Si–O bond and covalent Si–Si bond. HF molecule is polar, due to the large difference in electronegativity between H and F. A similar but less pronounced polarity exists when Si is bonded to O (but not in Si–Si bonds). As HF approaches a Si–O bond, the relatively positive H would be attracted by the relatively negative O, forming H_2O and leave the surface. After the complete removal of SiO_2 via HF wet etch, dangling bonds on the silicon surface would be bond to fluorine atoms, given the higher Si–F bond energy (6.0 eV) comparing to that of Si–H (3.5 eV). The ionic nature of Si–F bond would polarize the silicon back bond, making the surface silicon more positive and the atom underneath more negative. This asymmetric electron distribution allows the insertion of another HF molecule into the Si–Si bond, which in turn leads to the fluorination of the surface silicon and the hydrogenation of the silicon underneath. This process would repeat until the initial surface silicon is bonded by four fluorine atoms and leave the surface as SiF_4 , exposing the second layer with hydrogen termination [33, 34]. The transition from an F-terminated surface to an H-terminated surface is accomplished via the removal of one monolayer of

Table 2. Important energy threshold values for ion energies in plasma ALE of Si and SiO_2 .

	E_{mod} (eV) ^a	E_{des} (eV)	E_0 (eV)	Etch product	ALE window	Ref
Si	0	2.3	4.7	SiCl_2	40–60 eV	[38, 39]
SiO_2	0	—	5.0	SiF_4 , CO, CO_2	—	

^a For plasma-enhanced modifications, the barrier is considered negligible as plasma produces radicals, which readily react with surfaces.

fluorinated silicon atoms—essentially an atomic layer etching process. This particular study, although not focused on patterning sub-nanometer features, is the basis of an important general model of atomic layer etching: surface atom removal could be initiated by the polarization of surface bonding, which localizes electrons and creates a chemical contrast to the sub-surface layer (e.g. metal, where the electrons are delocalized and more evenly distributed).

Since surface modification (compositional control) is the critical first step, the use of plasmas should be considered as it has long been shown to be effective in modifying surface composition of various materials. Preferential sputtering is a commonly observed phenomenon during ion bombardment, where energy and momentum transfer, which are highly mass dependent, cause the incongruent removal of surface atoms. On the topic of whether mass or chemical bonding is more important to bombardment induced compositional change in alloys and oxides, however, it has been shown that chemical bonds play a more important role [36], which suggests that a chemical driving force during plasma exposure (with energetic ions) can be used to tailor and control the surface composition and chemical contrast [37].

Therefore, electron configuration and composition, two surface properties sensitively subjected to external influences, intentionally or inadvertently, can be effectively tuned to achieve a chemical contrast on a surface to be etched. Indeed, these minuscule parameters, when controlled properly, have been shown to enable etch selectivity in the gas phase by halogen-based plasmas between Si and SiO_2 , as shown in table 2, E_{mod} is the energy barrier for surface modification, and E_{des} is the energy barrier for removing the chemically modified material. The difference in surface binding energy (E_0) allows different etching chemistries to be implemented on Si (Cl-based) and SiO_2 (F-based), respectively. It is natural to think if the same concept can be applied to help realize etch selectivity between metal and metal oxides.

4. Metals versus metal oxides

Metals' generally low susceptibility to etching on atomic-scale partially shares the same origin as their advantageous attributes. Electrons in metal lattices can extend their range of movement over the physical size of the orbital provided by individual atoms, delocalize from their original atoms and form a so-called 'sea of electrons'. While such an attribute enables high electron mobility, it simultaneously makes atomic level etching more difficult, in which a single layer of atoms and its corresponding electrons need to be targeted, forming

a volatile compound, and then be removed. Metal oxides, on the other hand, has significantly different physical properties comparing to metals, chemical bonds in metal oxides tend to be ionic, which could account for their hardness and brittleness, whereas pure metals are usually soft and ductile. The ionic nature of metal-oxygen bonds originates from the relatively large differences in electronegativities between most metals and oxygen (1.5–2), electrons are favorably attracted to oxygen. Since the electrons tend to be more localized, metal oxides in general have inferior electrical conductance and are more prone to further reactions. At its core, the difference between metals and their oxides comes from whether valence electrons are delocalized and free to move in the lattices, or localized and bonded to neighboring non-metallic elements. It is possible to leverage the chemical contrast between metals and metal oxides to develop a generalized and selective chemical etching process, if the electron configuration and surface composition could be finely controlled.

Luckily, etching is not the only field that focus on metals' electron configurations and compositions, catalytic chemistry also devotes considerable amount of focus, although for very different reasons. Metals, especially transition metals, are widely considered as good catalysts for various reactions. Transition metals excel in this application due to their two-shell valence electron structure, in which electrons responsible for chemical reactions reside in not one, but two electron orbitals [40]. This particular electron configuration allows easier losing or gaining of electrons from other molecules, ultimately results in interchanging between different oxidation states. In catalysis, it is always ideal to maintain a clean, external-bond-free metal surface, in order to maximize the flexibility of electron bonding to different atoms. Deactivation of catalytic performance might occur as the consequence of one or more of the following causes: unwanted physisorption or chemisorption of foreign atoms on the catalyst surface; physical coverage of catalyst surfaces via change in morphology and/or agglomeration. In the broadest sense, deactivation process usually includes multiple reactions and is a combined effect of both physical and chemical loss of available surface sites. The term 'catalyst poisoning' is used to aptly describe the essence of the scenario. The concept of poisoning could be handily borrowed and repurposed in the development of etching processes, where the formation of surface metal-nonmetal bonds is ideal for establishing chemical contrast. Unlike the environment in which catalysts often located, the number of unwanted species is minimized in high vacuum systems used in fabricating integrated circuits, where nanometer level etching is carried out. The number of unintentional bond formation and unwanted reactions are thus avoided. Surface bonds could be formed controllably instead of inadvertently. In other words, metal surfaces could be purposefully 'poisoned' to localized valence electrons.

This 'intentional poisoning' approach can be particularly important for etching chemically inert metals such as Pd and Pt, which are chemically inert and etch-resistant but extensively used and studied as catalysts in vast number of reactions. While catalysts are commonly treated as spectators of reactions, they do participate in intermediate reactions and

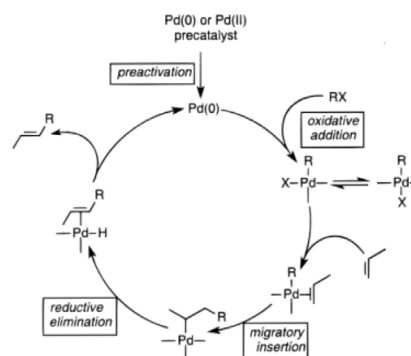


Figure 4. A simplified catalytic cycle for the Heck reaction, in which the oxidation state of Pd increases during oxidative addition and decreases during reductive elimination. Reprinted with permission from [41]. Copyright © 2000 American Chemical Society.

the oxidation state of noble metals is not constant throughout the catalytic cycle. They typically lower the reaction energy barriers via altering oxidation states and return to the original state in the final step. An example extensively studied in the field is the Heck reaction, which could be summarized in figure 4.

The Heck reaction could be summarized as the formation of a substituted alkene from unsaturated halide (or triflate) with an alkene in the presence of a palladium catalyst. One of the basic types of reactivity in palladium-driven catalytic cycles comes from the ability of Pd(0) species to undergo oxidative addition to various R–X bonds and the addition of thus formed R–Pd–X intermediates to unsaturated bonds. The R–Pd–X intermediates have more flexible electron configurations and could be attached to external ligands, undergoing the migratory insertion step. Finally, a new bond between carbons is formed and Pd is freed from the complex, available for the next cycle of catalysis. This is an extremely simplified discussion of this reaction scheme, but it nonetheless captures the importance of the oxidation state of Pd. While Pd is commonly regarded as inert and unreactive, the change of its oxidation state in the Heck reaction cycle is at core of realizing the subsequent reaction. The Heck reaction is one of many catalytic cycles to show the regeneration of catalysts, which means the full recovery of initial catalysts. But unlike many other catalytic cycles such as the Monsanto process or the Wacker process, where metalorganic complexes are used as catalyst, metallic Pd is used in the Heck reaction, and thus could provide potential insight in etching chemistry. If the intermediate R–Pd–X could be extracted and react with other targeted chemistry, the irrecoverable removal of Pd (not ideal for catalysis but beneficial in ALE) could be realized. Abundant literature exists for the formation of Pd intermediates, but subsequent intermediate removal still lacks in-depth study. The importance of oxidation state could also be seen in the synthesis of organometallic precursors for chemical vapor deposition (CVD) of noble metals such as Pd and Pt, where the metalorganic compounds need to be volatile, such as metal β -diketonates complexes [42]. Leveraging this knowledge, metal etching could be realized if the process leading to the formation volatile metal β -keto-hydrazoneates can be achieved on surfaces via the control of the oxidation states. A

systematic way of evaluating the feasibility of these reactions would provide insight on developing chemical etching processes that addresses both selectivity and directionality.

Now that the importance of oxidation state is addressed, the next question is how to manipulate the oxidation states of metals in a controlled manner. For ultra-thin (<3 nm) oxide on metal surfaces, Cabrera and Mott developed a theory characterizing the oxidation kinetics, starting with oxygen physisorption onto a surface [43]. For film thickness at which quantum tunneling effect is non-negligible, electrons could pass freely from the metal to the oxide surface to further ionize the physisorbed oxygen atoms. The accumulation of electrons at the surface would establish a constant field inside the oxide layer, eventually setting up a quasi-equilibrium between the metal and the adsorbed oxygen. Oxide formation would terminate once the equivalent amount of charge is moved in the opposite direction via metal ion diffusion. Therefore, if a chemical driving force during plasma exposure (with energetic ions) can be used to tailor and control the surface oxidation states, the resulting chemical contrast may be leveraged to realize ALE.

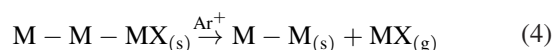
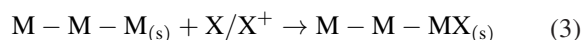
5. Role of energetic ions in modification and removal

Based on concepts developed for RIE, plasma ALE utilizes energetic ions for both surface modification and subsequent removal. The modification step (denoted by step A) self-terminates with the entire occupation of available surface sites for chemisorption. The removal step (denoted by step B) self-terminates with the complete removal of modified region, which has lower bonding energy with the underlying layer. The etching anisotropy comes from the directionality of ions in both modification and removal steps. In addition to the chemical selection, which is material dependent, the major parameter to adjust etching characteristics is the ion energy. A recent review summarized the ideal operating energy window for both steps, as shown in equation (2) [39]:

$$E_{\text{mod}} < \varepsilon_A < E_{\text{des}} < \varepsilon_B < E_0 \quad (2)$$

where E_{mod} is the energy barrier for surface modification, while E_{des} and E_0 are the energy barriers for removing the chemically modified and bulk material, respectively. The energies ε_A and ε_B are delivered to the surface in steps A and B to overcome these barriers based on chosen process. A selected list of materials studied using the aforementioned guideline is compiled in Table 3.

The overall reaction pathway for this type of plasma ALE could be summarized as the following:



where M is the pristine metal, MX is the chemically modified metal, X/X^+ and Ar^+ are neutrals and ions used for modification and removal, respectively. Here, a note should be made that, during plasma exposure in (3), inevitably some ions

Table 3. Important energy threshold values for ion energies in plasma ALE of selected materials.

	E_{mod} (eV) ^a	E_{des} (eV)	Etch product	Calculated E_0 (eV) [39]	ALE window [39]
Ge	0	—	GeCl_2 , GeCl_4 ^b	3.8	20–30 eV
C	0	—	CO , CO_2 ^b	7.4	35–75 eV
W	0	—	WCl_6 ^b	8.9	—
GaN	0	—	GaCl_3 , N_2 ^b	8.6	50–90 eV
Ta	0	0.6	TaCl_5	8.1	20–90 eV

^a For plasma-enhanced modifications, the barrier is considered negligible as plasma does the work of dissociating reactants into radicals prior to adsorption.

^b Etch products were not specified in the original publication, but these are likely products based on the discussion of the publication.

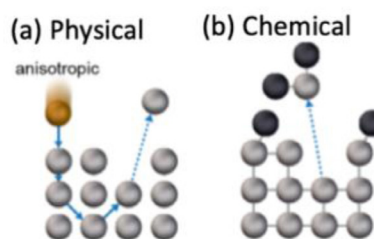
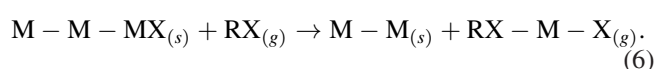
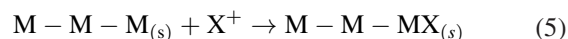


Figure 5. Comparison of different methods to overcome the surface binding energy, E_0 , including via (a) kinetic energy from collisions and/or (b) chemical bonds that lower E_0 . Adapted with permission from [38]. Copyright © 2018 American Chemical Society.

would impact on the surface. However, since the neutral-to-ion ratios are usually larger than 10, considerable of the chemical modification is due to reactions with neutrals. Ar^+ only serves as sputtering source and it is not a part of a chemical process. It is noted that while halogen chemistry is predominantly used during the modification step, the X notation shall not be limited to halogen atoms. The window of selectivity could be small for plasma ALE, if the surface binding energy difference of pristine target material and its halide is insignificant, thereby imposing a constraint on the control of the kinetic energy of Ar^+ ions. As shown in table 2, difference in surface binding energy between Si and SiCl_2 is about 2.4 eV, which results in a narrow ALE window of 20 eV. Additionally, considering the energy spread in most ion sources, ions with higher energies could inevitably introduce uncontrollable sputtering of the non-modified layer.

To address this problem, this review suggests an alternative pathway for creating and removing the modified layer, where chemical ions from plasma is used to enable the conversion of the surface layer and exerts the reaction directionality, while another chemical reagent (e.g. organic molecule) is used in the second half-reaction to isotropically tackle the chemically converted surface layer with high selectivity:



A quick inspection of reaction sets (3), (4) and (5), (6) could lead to the conclusion that, while the removal process differs between the two approaches, both are capable of

Table 4. Calculation of Gibbs free energy of reactions of etching reactions between six elements (metallic state and oxides) and BCl_3 , calculation done for 1 atm, 25 °C.

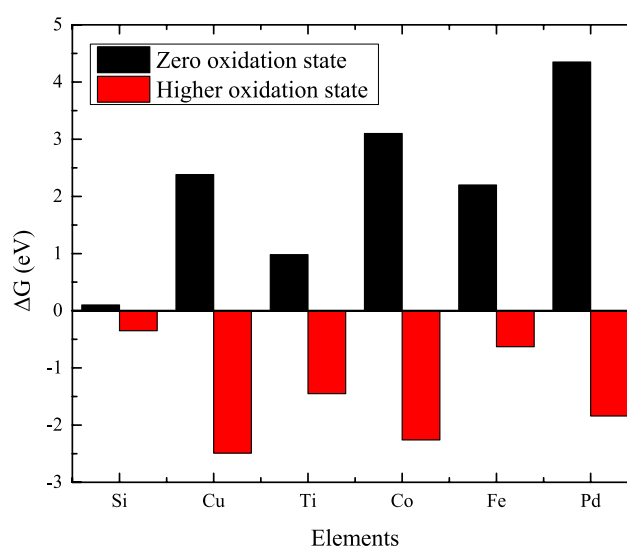
Element		Reaction	ΔG (eV)
Si	Si	$\text{Si}_{(s)} + 4 \text{BCl}_{3(g)} \rightarrow \text{SiCl}_{4(g)} + 2 \text{B}_2\text{Cl}_{4(g)}$	0.10
	SiO_2	$1.5 \text{SiO}_{2(s)} + 3 \text{BCl}_{3(g)} \rightarrow 1.5 \text{SiCl}_{4(g)} + (\text{BOCl})_{3(g)}$	−0.35
Cu	Cu	$3\text{Cu}_{(s)} + 3\text{BCl}_{3(g)} \rightarrow \text{Cu}_3\text{Cl}_{3(g)} + 1.5\text{B}_2\text{Cl}_{4(g)}$	2.38
	CuO	$3\text{CuO}_{(s)} + 3\text{BCl}_{3(g)} \rightarrow \text{Cu}_3\text{Cl}_{3(g)} + (\text{BOCl})_{3(g)} + 1.5\text{Cl}_{2(g)}$	−2.49
Ti	Ti	$\text{Ti}_{(s)} + 4\text{BCl}_{3(g)} \rightarrow \text{TiCl}_{4(g)} + 2\text{B}_2\text{Cl}_{4(g)}$	0.98
	TiO_2	$1.5\text{TiO}_{2(s)} + 3\text{BCl}_{3(g)} \rightarrow 1.5\text{TiCl}_{4(g)} + (\text{BOCl})_{3(g)}$	−1.45
Co	Co	$2\text{Co}_{(s)} + 4\text{BCl}_{3(g)} \rightarrow \text{Co}_2\text{Cl}_{4(g)} + 2\text{B}_2\text{Cl}_{4(g)}$	3.10
	Co_3O_4	$\text{Co}_3\text{O}_{4(s)} + 4\text{BCl}_{3(g)} \rightarrow 1.5\text{Co}_2\text{Cl}_{4(g)} + 4/3(\text{BOCl})_{3(g)} + \text{Cl}_{2(g)}$	−2.26
Fe	Fe	$2\text{Fe}_{(s)} + 4\text{BCl}_{3(g)} \rightarrow \text{Fe}_2\text{Cl}_{4(g)} + 2\text{B}_2\text{Cl}_{4(g)}$	2.20
	Fe_2O_3	$\text{Fe}_2\text{O}_{3(s)} + 3\text{BCl}_{3(g)} \rightarrow \text{Fe}_2\text{Cl}_{4(g)} + (\text{BOCl})_{3(g)} + \text{Cl}_{2(g)}$	−0.63
Pd	Pd	$\text{Pd}_{(s)} + 2\text{BCl}_{3(g)} \rightarrow \text{PdCl}_{2(g)} + \text{B}_2\text{Cl}_{4(g)}$	4.35
	PdO	$3\text{PdO}_{(s)} + 3\text{BCl}_{3(g)} \rightarrow 3\text{PdCl}_{2(g)} + (\text{BOCl})_{3(g)}$	−1.84

removing one atomic layer of metal and generating an atomically clean surface. A subtle yet important distinction between (3) and (5) is the relative importance of neutrals (X) and ions (X^+). In most plasma systems, the neutral-to-ion ratios can be adjusted and the ion energies can be controlled. For this process to be most effective, an ion beam source can be used with tailored ion flux and energy. The major deviation is thus the removal step, where in (6) an organic molecule is used to thermally react with the modified layer instead of physically bombard the surface with ions. Conceptually this has been previously shown in another review where both physical and chemical processes are identified as viable means to reduce surface binding energy and thus facilitate the removal of surface atoms, as shown in figure 5.

The final result would be identical, with underlying pristine metal layer getting revealed. The different reaction intermediate, however, might allow new reaction pathways to be realized to achieve better etch selectivity and anisotropy. For the proposed chemistry to work, it is critical to consider whether there exist chemistries that solely target the modified metal and does not react with the pristine metal. It is possible that thermodynamic assessment can be used to perform such analysis.

6. Role of thermodynamic evaluation in predicting reaction chemistry

In contrary to ALE based on equations (3) and (4), which relies on ion energy for removal, thermal ALE utilizes the reaction favorability between tailored and untailored layers to selectively remove atoms, in those cases, thermodynamics is heavily leveraged to predict reaction feasibilities. To perform informed thermodynamic calculations and simulations of its behavior in various chemical and physical environments, it is essential to obtain standardized thermodynamic data the material and potential reactants presented in the environment. For some of the well-studied material systems, such as silicon in halogenic environments, abundant literature exists for systematic studies. For most of other less characterized materials and chemistries, however, classic experimental thermodynamic

**Figure 6.** Plot of calculation of Gibbs free energy of reactions of etching reactions between six elements (zero versus higher oxidation states) and BCl_3 , calculation performed at 1 atm, 25 °C.

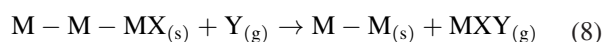
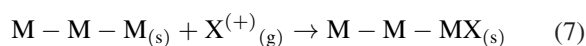
studies and measurements were significantly outpaced by the rapid development in the applications, and little data are available. In particular, very few theoretical thermodynamic studies were done on plasma ALE, due to the intrinsic difficulty of modeling non-equilibrium reactions. Nonetheless, a thorough analysis of the equilibrium reactions is useful if a hybrid plasma-thermal ALE approach is to be developed.

By definition, investigating the thermodynamics of a certain reaction means to assess whether, under a given set of external conditions such as temperature and pressure, the prescribed reaction might occur. In a more practical sense, one usually evaluates the change in Gibbs free energy, $\Delta G = \sum_i n_i \mu_i$, for the proposed reaction, where n_i is the stoichiometric coefficient (taken as negative for reactants) and μ_i is the chemical potential of the i th species, respectively. If the change is calculated to be negative under the given conditions, the proposed reaction will occur spontaneously, and the reaction is considered as thermodynamically favorable. Otherwise, the material is stable under the given physical and chemical environment

Table 5. Reported ALE chemistries on metal oxides (no chemistry reported on corresponding metals) and metals (require oxidation as modification).

Materials		Modification	Removal	Ref	Comment
Metal oxides	HfO ₂	BCl ₃	Ar	[23]	Metallic state ALE Possible via oxidation
	ZnO	Acetylacetone	O ₂	[24]	
	TiO ₂	BCl ₃	Ar	[25]	
	Al ₂ O ₃	Sn(acac) ₂	HF	[44]	
Metals	W	O ₂ followed by BCl ₃	HF- pyridine	[7]	Oxidation step required for ALE
	Co	O ₂	HCOOH	[45]	
	Pt	O ₂	HCOOH	[45]	
	Cu	O ₂	HCOOH	[45]	

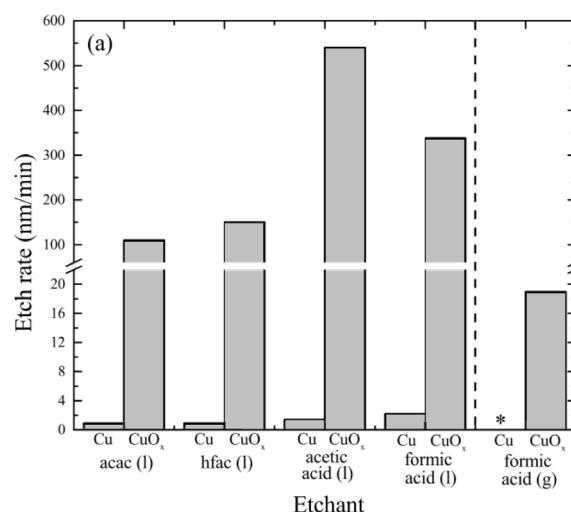
and the reaction is considered as thermodynamically unfavorable. In the context of ALE, where the etching process could be divided into controlled modification and removal stages, generalized reactions could be evaluated as the following two half-cycle reactions, which are slightly different from equations (3)–(6) to make them more general:



where M–M–M and M–M represent the initial and final structure of the targeted material, MX and MXY are its modified surface states and etching products, X⁽⁺⁾ is the modification reactant (which can be an ion or a neutral) and Y is the removal reactant (that could be Ar⁺ or RX). It is important to point out that, to have a well-controlled process that allows self-limiting reactions on the surface, the modified states (MX) need to be in the solid phase, still binding to the bulk to avoid exposing the underlying pristine layer and losing the self-limiting reaction. The etching product (MXY), on the other hand, must be in the gas phase to realize the etching of the solid, therefore the volatility of MXY should be assessed carefully.

To illustrate the importance of oxidation state in the context of reaction thermodynamics, a commonly used and well-documented etchant, BCl₃, is used to evaluate the etching of different pairs of materials. This evaluation could be considered as a particular case of reactions (7) and (8) where X is O and Y is BCl₃. Using tabulated data from HSC software, calculation of Gibbs free energy of reactions of etching reactions between six elements (zero versus higher oxidation states) and BCl₃ is shown in table 4 and figure 6.

It is clear that all oxides considered react much more favorably with BCl₃, when compared to their elemental counterparts. None of the reactions with zero oxidation states is spontaneous under the given conditions, whereas all of the reactions with oxides are spontaneous. This drastic difference shows how important and beneficial it is to control the oxidation state of surface elements, in order to realize selective removal of the modified layer. Like the case made in the previous section for the Si/SiO₂ system, where etching selectivity is realized from the change in oxidation states, a metal/metal oxide system could also benefit from this chemical contrast. Multiple pieces of literature from different groups have demonstrated oxidation as a necessary starting point for ALE, as listed in table 5. Also included in this table is selected work on ALE of selected metal oxides, given the relative easiness of

**Figure 7.** Etch rates of Cu and CuO_x in liquid phase acac, hfac, acetic acid, and formic acid are shown as measured at 80 °C. Reprinted from [46], with the permission of AIP Publishing.

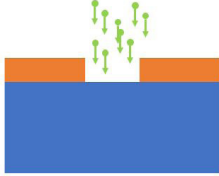
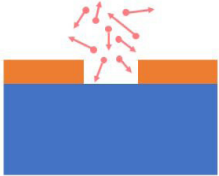
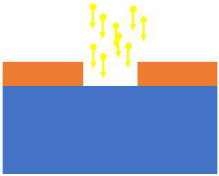
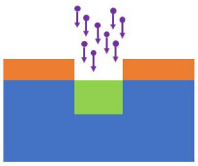
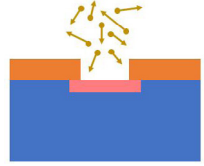
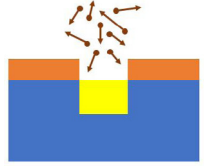
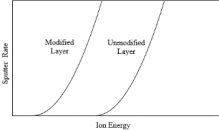
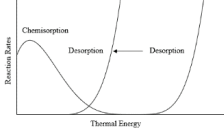
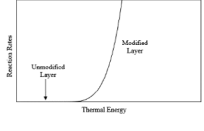
oxidizing metals using plasma, ALE pathways are predicted for metal oxides with existing ALE chemistries.

For example, a systematic study of the effect of oxidation state on etch rate selectivity was done on the Cu/CuO_x system with different organic etchants, in both liquid and gas phases [46]. It was tested that acac and hfac solutions were able to etch copper at a very small rate of 0.9 nm min^{−1}. Slightly higher etch rates of copper were observed in acetic acid (1.4 nm min^{−1}) and formic acid (2.2 nm min^{−1}) solution. The low etch rates indicate that the corresponding etch rates in the gas phase would be negligible due to the much lower concentration. Indeed, all four organic chemistries were used in the vaporizer system referenced [47]. No measurable etch rates were found for these organic vapors reacting with metallic copper at 80 °C (data not shown). Oxidized copper was etched at the rate of ~20 nm min^{−1}, yielding very high selectivity in gas phase. As shown in figure 7, controlled oxidation of Cu resulted in ~50 × increase in etch rate using tested organic etchants, implying an etching selectivity of ~50 of CuO_x over Cu in solution phase, and near infinite selectivity in gas phase.

7. Achieving etching selectivity and directionality simultaneously

From the previous comparison, both plasma ALE and thermal ALE have trade-offs. Plasma ALE grants both selectivity and

Table 6. Comparison between plasma ALE, thermal ALE and hybrid plasma-thermal ALE processes.

		Plasma ALE	Thermal ALE	Plasma-thermal ALE
		Plasma modification	Chemical modification	Plasma modification
Half-reactions		Ion sputtering	Chemical etching	Chemical etching
Modification	Chemical contrast formation	Chemisorption of halogen atoms via plasma 	Conversion to oxides via thermal reactions 	Conversion to oxides via plasma 
	Control parameters	Plasma chemistry	Reactant pressure/temperature	Ion chemistry and energy
Origin of selectivity		Difference in surface binding energy 	Difference in reaction favorability 	Difference in reaction favorability 
Removal	Etch product formation	Physical, anisotropic 	Chemical, isotropic 	Chemical, isotropic 
	Control parameters	Argon ion energy 	Pressure, temperature 	Pressure, temperature 
Origin of anisotropy		Directionality of Ar ⁺ 	Isotropic 	Chemical contrast 
Comments	ALE Window	Narrow, ion energy sensitive	Wide, determined by thermodynamics	Wide, determined by thermodynamics
	Control of selectivity and anisotropy	Both, in separate steps	Selectivity control only	Both, in single step

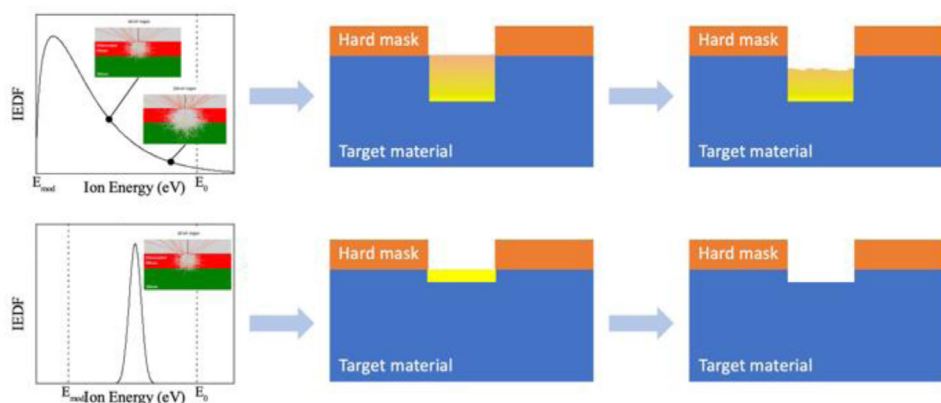


Figure 8. Ion energy distribution function (IEDF) in conventional plasma results in modified layer with over one atomic layer thickness and concentration gradient, which leads to non-uniform removal (top), IEDF of monoenergetic ion source results in monolayer modification and no concentration gradient, which leads to uniform, single layer removal (bottom). IEDF plots include simulation of 100 incident argon ions and the corresponding collision cascade into a silicon substrate and surface chlorinated silicon. Argon ion energies of 60 and 200 eV are simulated. The depth of chlorination is 1.0 nm. Adapted from [49], with the permission of AIP Publishing.

anisotropy but requires separate control of individual steps, both are highly energy sensitive with sometimes narrow ALE windows. Thermal ALE leverages fine-tuned overall thermodynamics to enable new reaction pathways, this comes with the cost of elevating reaction temperature, which might not be acceptable for reaction scheme with limited thermal budgets; it also sacrifices the control over anisotropy, given the random-motion nature of neutral particle movements. This review proposes a generalized hybrid plasma-thermal approach for ALE that combines the advantages from both the effect of ions and chemistry. The comparison between the three approaches can be summarized in table 6.

As can be seen in table 6, the source of selectivity and anisotropy in the hybrid plasma-thermal ALE process is identical: difference in reaction favorability in the removal step. This has the advantage of only requiring control of ion energy during the modification step, once the chemical contrast is established, subsequent removal would only be allowed thermodynamically on the tailored region, anisotropy is intrinsically maintained. On top of that, directionality is not required in the removal step, since previous chemical contrast would inherently guarantee proper etch stop on the sides. By comparison, ALE conditions in this plasma-thermal-based etching chemistries are much more forgiving comparing to plasma ALE setups since temperature and pressure are relatively easy to control than ion energies. The self-limiting characteristic of the proposed reaction scheme comes from the selectivity between the target material and its surroundings, which is dictated by the difference in thermodynamic favorability that could be determined by means introduced previously. The difference in thermodynamic favorability of different materials when exposed to the same chemistry could be leveraged to serve as reaction gateways to enable selective removal of target materials.

If the hybrid plasma-thermal ALE process is to be implemented, the modification step would be of crucial importance, as the quality of this step would determine both selectivity and anisotropy for subsequent removal chemistry. Current computational work on argon sputtering of modified layer

utilizes Monte Carlo-based simulation, the stochastic nature of the process always results in a distribution of incoming ion cascades. This means ion penetration and sputtering could never realize single atomic layer precision, even with fixed specified ion energy. This effect would limit the validity of simulation result, since experimental outcome would be a statistical average of the simulation of single ions, as illustrated in figure 8. Since current mainstream plasma reactors usually produce ions with energy distribution of tens of electron volts, multiple layers in the target material would be affected with a depth-dependent modification profile. Not only does multilayer treatment nonideal for layer-by-layer processes, depth-dependent exposure to incoming ions would cause uneven removal in subsequent cycles. Plasma source with the capability of producing consistent, monoenergetic ions could largely alleviate the issue. As shown in figure 8, sample treatment would have better control in terms of both modified layer depth and concentration. The adoption of monoenergetic ion sources would also benefit from the cross-examination of existing results from numerical simulation, in which ions with single energy is usually modeled [48]. Additionally, as detailed in table 2, existing literature claims that there is no energy barrier for adsorption since incoming reactants are fully dissociated and turned into radicals by plasma before being in contact with the surface. This assumption, if valid, suggests the role of ionized molecules be limiting since energy barriers do exist for the further dissociation and ionization of partially (or fully) ionized molecules. This lost portion of efficiency could be recovered by adopting a monoenergetic ion source, where non-zero modification threshold could be surmounted.

8. Summary

To better incorporate metals and leverage their superior properties in future nanoelectronics, a hybrid plasma-thermal ALE approach is discussed in this review in patterning them. The proposed approach does not depend on the difference of

surface desorption energy between modified and non-modified layer, as in plasma ALE; nor does it sacrifice directionality, as in thermal ALE. More specifically, oxidation by energetically controlled ions is suggested as the modification step and an organic ligand exposure is suggested as the removal step. Reaction thermodynamics could provide the necessary information to select the proper chemistry in creating the chemical contrast and in removing the modified surface layers. Other modification chemistries, i.e. nitridation, sulfurization, etc, could also be viable in creating chemical selectivity, as long as a corresponding material's removal chemistry can be identified. This hybrid plasma-thermal ALE approach has more experiment parameters that can be tuned to realize a chemically selective, yet directional, etching profile of a wider range of metallic materials.

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