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# Selection Criteria for Small-Molecule Inhibitors in Area-Selective Atomic Layer Deposition: Fundamental Surface Chemistry Considerations

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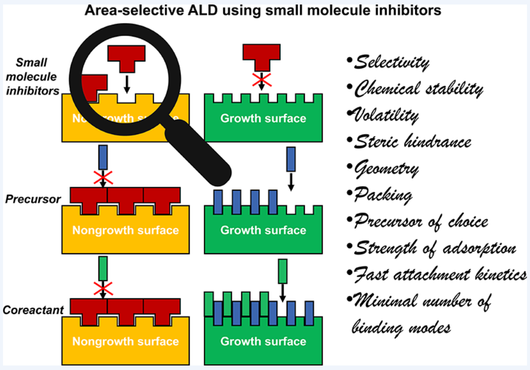

**CONSPECTUS:** Atomically precise and highly selective surface reactions are required for advancing microelectronics fabrication. Advanced atomic processing approaches make use of small molecule inhibitors (SMI) to enable selectivity between growth and nongrowth surfaces. The selectivity between growth and nongrowth substrates is eventually lost for any known combinations, because of defects, new defect formation, and simply because of a Boltzmann distribution of molecular reactivities on surfaces. The selectivity can then be restored by introducing etch-back correction steps. Most recent developments combine the design of highly selective combinations of growth and nongrowth substrates with atomically precise cycles of deposition and etching methods. At that point, a single additional step is often used to passivate the unwanted defects or selected surface chemical sites with SMI. This step is designed to chemically passivate the reactive groups and defects of the nongrowth substrates both before and/or during the deposition of material onto the growth substrate. This approach requires applications of the fundamental knowledge of surface chemistry and reactivity of small molecules to effectively block deposition on nongrowth substrates and to not substantially affect deposition on the growth surface. Thus, many of the concepts of classical surface chemistry that had been developed over several decades can be applied to design such small molecule inhibitors. This article will outline the approaches for such design.

This is especially important now, since the ever-increasing number of applications of this concept still rely on trial-and-error approaches in selecting SMI. At the same time, there is a very substantial breadth of surface chemical reactivity analysis that can be put to use in this process that will relate the effectiveness of a potential SMI on any combination of surfaces with the following: selectivity; chemical stability of a molecule on a specific surface; volatility; steric hindrance, geometry, packing, and precursor of choice for material deposition; strength of adsorption as detailed by interdisplacement to determine the most stable SMI; fast attachment reaction kinetics; and minimal number of various binding modes.

The down-selection of the SMI from the list of chemicals that satisfy the preliminary criteria will be decided based on optimal combinations of these requirements. Although the specifics of SMI selection are always affected by the complexity of the overall process and will depend drastically on the materials and devices that are or will be needed, this roadmap will assist in choosing the potential effective SMIs based on quite an exhaustive set of "SMI families" in connection with general types of target surfaces.

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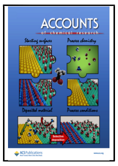

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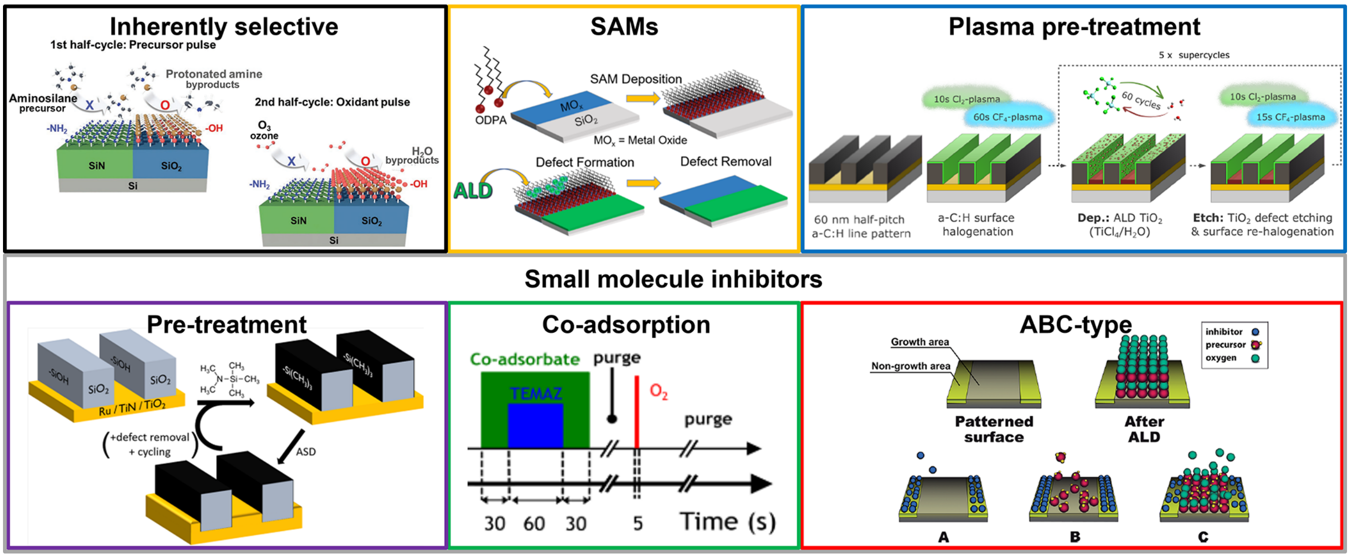

**Figure 1.** State of the art for AS-ALD. Top panel, from left to right: inherently selective ALD; self-assembled-monolayers (SAM); plasma pretreatments. Bottom panel, small molecule inhibitors (SMIs) that can be dosed by the vapor phase. From left to right: SMIs used to chemically passivate the NGS before the ALD process and during the ALD process either by codosing precursor and SMI (coadsorption) or as an additional step of the ALD cycle. [Images reproduced with permission from refs 21 (Copyright 2021, Wiley−VCH GmbH), 3 (Copyright 2017, American Chemical Society), 17 (Copyright 2019, American Chemical Society), 19 (Copyright 2020, American Chemical Society), 22 (Copyright 2021, American Chemical Society), and 13 (Copyright 2020, AIP Publishing).]

*with incoming ALD precursor molecules were considered. A quantitative analysis of steric and electronic factors determining these interactions was proposed.*

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- Merkx, M. J. M.; Angelidis, A.; Mameli, A.; Li, J.; Lemaire, P. C.; Sharma, K.; Hausmann, D. M.; Kessels, W. M. M.; Sandoval, T. E.; Mackus, A. J. M. Relation between Reactive Surface Sites and Precursor Choice for Area-Selective Atomic Layer Deposition Using Small Molecule Inhibitors. *J. Phys. Chem. C* **2022**, *126*, 4845−4853.[4] *Effects of precursor, processing temperature and type of surface hydroxyl groups on precursor blocking by small molecule inhibitors are investigated by Fourier transform infrared spectroscopy. We generalize how these additional knobs can be used for improving the selectivity.*

## 1. INTRODUCTION

Understanding chemical reaction mechanisms has always been the key to developing new chemical technologies. Within the past decade, atomic- and molecular-level understanding of chemical processes at surfaces, what used to be considered a very fundamental field of science, found its way directly into applications and devices, as the manufacturing approached the level of miniaturization requiring atomic-level precision. Nanoscale manipulation of materials to exert control over feature shape and size, and their integration into a functional device has become the cornerstone of nanotechnology fabrication.[5] For decades, this has mostly been achieved by *top-down* fabrication processes, where deposition, lithography, and etching cooperate to chisel patterned materials on a surface, and by iterating these processes, functional devices are built. With the ever-shrinking dimensions of the features employed, for example, in semiconductor manufacturing, complications for such iterative processes start to arise,[6] and complementary *bottom-up* methods are developed to circumvent these issues and/or expand the processing window. For example, area-selective deposition (ASD) can be put into use to aid top-down fabrication in fully self-aligned vias.[7,8] Other application examples include ASD on photoresist, contact over gate structure, bottom-up filling,[9] selective hard-mask and etch-stop layer depositions, which have been discussed in detail by G. N. Parsons and R. D. Clark in a recent review on ASD.[5]

Many of the methods described for *atomically precise* manufacturing rely heavily on atomic layer deposition (ALD) as a key processing step. ALD is a layer-by-layer deposition method that allows for atomic-level thickness control, conformality on 3D structures, and large-area uniformity. In its most simple expression, ALD relies on the cyclic and alternating exposures of a substrate to a precursor and a coreactant that undergo self-limiting surface reactions.[10] Because of its nature, ALD can offer optimal opportunities to control each individual surface reaction at the atomic level and thus achieve area-selective ALD (AS-ALD).[11−13]

AS-ALD is based on dramatic differences in chemical reactivity between the substrate regions with surface groups that promote growth of thin films (growth surfaces, GS) and chemically nonreactive surface regions (nongrowth surfaces, NGS). If sufficiently large differences in thermodynamics or kinetics of surface reactions exist on GS vs NGS, selective deposition can be naturally obtained, referred to as inherently selective ALD.[14,15] However, such combinations are rare, and the GS and NGS must be chemically modified through selective manipulation of surface functional groups to either

Table 1. Nonexhaustive Overview of SMIs and AS-ALD Processes Employing SMIs

| SMIs[a] | GS | NGS | deposited material | ref(s) |
|---|---|---|---|---|
| thiols[b] | $SiO_2$; TiN; W | Cu | Ru | 23, 24 |
| alcohols[c] | $SiO_2$ | $Al_2O_3$ | $SiO_2$ | 25 |
| carboxylic acids[c] | $SiO_2$ | ZnO; $TiO_2$; IGZO; $SnO_2$ | $SiO_2$ | 26 |
| alkyne[d] | $ZrO_2$; $SiO_2$ | Cu | $ZrO_2$ | 13 |
| $\beta$-diketones[c] | $SiO_2$; $GeO_2$; $WO_3$; $WS_2$; $TiS_2$ | $Al_2O_3$; $HfO_2$; $ZrO_2$; $TiO_2$; $NbS_2$; $Nb_2O_5$; $MoO_3$; $MoS_2$ | $SiO_2$; $WS_2$ | 3, 27, 28 |
| aromatic amine[c] | $SiO_2$; TiN; $Al_2O_3$ | Co; Ru | TiN | 29 |
| aminosilanes[b] BDMADMS, DMATMS | $Al_2O_3$ | $SiO_2$ | $Al_2O_3$ | 30 |
| methoxysilanes[b] | Cu | $SiO_2$ | $Al_2O_3$ | 31 |
| aminosilane DEATMS | $SiO_2$; TiN | Si−H; W | Ru | 32 |
| aminosilanes BDMADMS + DMATMS | SiN | $SiO_2$ | $Al_2O_3$ | 33 |

[a] BDMADMS = bis(dimethylamino) dimethylsilane; DMATMS = dimethylaminotrymethylsilane; TMPS = trimethoxypropylsilane; DEATMS = (*N*,*N*-diethylamino) trimethylsilane. [b] SMIs are employed as pretreatment [c] SMIs are employed in ABC-type cycles. [d] SMIs are coinjected with the precursor.

allow or inhibit the deposition chemistry.[5,16] Most of the time, in AS-ALD, the target of chemical modification is the NGS, where chemical functionalization is used to prevent film deposition. Such modification can be performed either prior to the ALD process, for example using self-assembled monolayers,[17] plasma or small molecule inhibitor (SMI) surface modification,[18,19] or during the ALD process, by inserting SMIs either by coinjection or as a separate step in the ALD cycle.[3,13] Figure 1 provides a concise mechanistic overview of the different AS-ALD routes. Herein, we focus on approaches that make use of SMIs.

The role of SMIs is analogous to the role of protective groups in organic chemistry, where, for performing a selective chemical reaction at a specific reactive site, other reactive sites are blocked using protective groups. Similarly to a set of requirements for a “good” protective group, several requirements for SMIs must be fulfilled for their successful implementation.[20]

Although the need for a definitive set of requirements for selecting appropriate SMIs in a variety of processes is obvious, the ever-increasing number of applications of this concept still rely on trial-and-error, while at the same time, there is a substantial breadth of surface chemical reactivity analysis and concepts of classical surface chemistry that can be applied for designing/selecting effective SMIs and thus accelerate developments in the field of AS-ALD.

Herein, we made an early attempt at outlining the rationale for such design/selection by discussing critical concepts such as those listed below:

- selectivity;
- chemical stability on a specific surface;
- volatility;
- steric hindrance, geometry, packing, and precursor of choice;
- strength of adsorption;
- fast attachment reaction kinetics; and
- minimal number of various binding modes.

## 2. BASIC REQUIREMENTS AND PRELIMINARY CRITERIA FOR SMI PROPERTIES

### 2.1. Selectivity

Table 1 provides a nonexhaustive overview of SMIs, GS and NGS, which will serve as a basis to derive generic trends on the selectivity conferred by different types of SMI, based on their reactive group.

General trends can be derived from Table 1 for different GS and NGS:

(i) Inhibiting metals vs oxides: thiols, alkyne, aromatic amine
(ii) Inhibiting oxides/sulfides vs other oxides/sulfides: carboxylic acids, $\beta$-diketones
(iii) Inhibiting oxides vs metals: methoxysilanes

**(i, a)** For thiol SMIs, the driving mechanism for passivation of metals vs oxides is the formation of a strong metal−sulfur bond (e.g., 274 kJ/mol for Cu−S).[34] Thiols can chemisorb to produce thiolates at a surface, according to eq 1. The reaction is further stabilized by the formation of a hydrogen−metal species that can subsequently recombine with other hydrogen atoms and desorb as $H_2$:

$$^{*}\mathrm{M} + \mathrm{RSH} \rightarrow {}^{*}\mathrm{M{-}SR} + {}^{*}\mathrm{M{-}H} \qquad (1)$$

where the asterisk symbol (*) denotes the surface species.

On the basis of thermodynamics, potential NGS can be Ti (Ti−S, 418 kJ/mol), Co (Co−S, 397 kJ/mol), or Ni (Ni−S, 356 kJ/mol). A similar reaction, however, is less likely to take place on metal oxides because of energetic reasons: a generally strong M−O bond must be broken as described in eq 2.

$$^{*}\mathrm{M{-}OH} + \mathrm{RSH} \rightarrow {}^{*}\mathrm{M{-}SR} + \mathrm{H_2O} \qquad (2)$$

where the asterisk symbol (*) denotes the surface species.

By comparing the bond dissociation energies of various metal−oxygen bonds, one can gauge whether reaction 2 is likely to occur. It has been shown that methanethiol can chemisorb on $In_2O_3$ and ZnO (In−O = 346 and Zn−O = 250 kJ/mol),[34] which form less strong metal−oxygen bonds than $SiO_2$ and $Al_2O_3$ (Si−O = 799 and Al−O = 501 kJ/mol).[24,34] Based on the study of Grimm et al., potential GS can be $Al_2O_3$, $CeO_2$, $Fe_2O_3$, NiO, $WO_3$, $ZrO_2$, and NGS (besides metals): ZnO and $In_2O_3$.[24]

**(i, b)** Alkyne and aromatic amines are characterized by $\pi$-bonds that can strongly interact with partially filled *d*-orbitals of metal surfaces and potentially rearrange on the surface to form stable chemisorbed (or very strongly physisorbed) products.[13,35] Conversely, on metal oxides, a weak hydrogen bonding can occur and the physisorbed molecule can easily desorb from these surfaces. However, at low temperature (20 °C), metal oxides with strong Lewis acid sites, e.g., $Al_2O_3$ and $Ga_2O_3$, can activate the C−H bond leading to chemisorbed acetylides, which underlines possible exceptions and diverse chemical interaction modes.[36] Such reactions have been reported to happen to a lower extent on CaO and MgO and not at all on $SiO_2$ and $TiO_2$.

**(ii)** Carboxylic acids and $\beta$-diketones are thought to chemisorb on metal oxides having predominantly OH groups with Brønsted basic character and not on those having OH functionalities with mostly acidic character. The chemisorption reaction can be thought of as an acid−base reaction, as described in eq 3.

$$\text{RCOOH} + {}^{*}\text{M–OH} \rightarrow {}^{*}\text{RCOO–M} + \text{H}_2\text{O} \qquad (3)$$

where the asterisk symbol (*) denotes the surface species.

The acidity of the SMIs, with respect to the basicity of surface hydroxyl groups, can be used as a rule of thumb to predict whether these types of SMIs will chemisorb on the surface. While $SiO_2$ has mostly acidic OH groups, ZnO or $Al_2O_3$ have more basic character, compared to $SiO_2$, which explains the selective growth of $SiO_2$ on $SiO_2$ and not on $Al_2O_3$ or ZnO when using acetylacetone (Hacac) as SMI.[3,26,27] The relative acidity of metal oxides surfaces based on the Sanderson's electronegativity was employed by Mameli et al. to rationalize the selective chemisorption of Hacac, as summarized in Figure 2.[3]

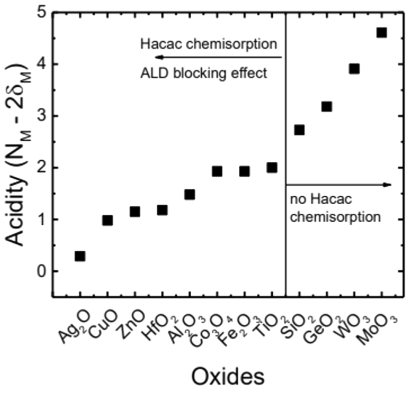


**Figure 2.** Surface acidity for diverse metal oxides, calculated following the method described in ref 37. $N_M$ is the formal oxidation state of the metal cation M, and $\delta_M$ is the Sanderson's partial charge on the metal M in the oxide compound. The vertical line separates the materials depending on whether Hacac chemisorption is expected or not. [Reproduced with permission from ref 3. Copyright 2017, American Chemical Society.]

To approach a more realistic description of surface reactivity, one must consider that each metal oxide has several types of hydroxyl groups and depending on the coordination and the proximity of other functional groups and the extent of hydrogen bonding, the hydroxyls of a single surface may have a range of different acidic/basic character and thus different reactivity.

**(iii)** Methoxysilanes of general structure $Si(R)_{4-x}(OCH_3)_x$, and particularly, trimethoxypropylsilane (TMPS), have been shown to confer selectivity between Cu (GS) and $SiO_2$ (NGS), when depositing $Al_2O_3$.[31] Such selective inhibition has been rationalized in terms of presence/absence of proton-donating groups at the surface. $SiO_2$ has acidic hydroxyl groups, which can donate a proton to hydrolyze the methoxy groups of the SMI. On the other hand, a metallic surface like Cu lacks proton-donating groups.

The general reaction is shown in eq 4:

$$\begin{aligned} &{}^{*}\text{Si–OH} + \text{Si(R)}_{4-x}(\text{OCH}_3)_x(g) \\ &\quad \rightarrow {}^{*}\text{Si–O–Si(R)}_{4-x} + \text{CH}_3\text{OH}(g) \qquad x \le 4 \qquad (4) \end{aligned}$$

We expect such reaction to be extendable to other GS and NGS combinations with similar characteristics, i.e., NGS has proton-donating groups (Brønsted acid), while GS does not.

From the examples above, the selectivity can be rationalized by considering the acidity/basicity of surfaces with respect to a possible SMI, i.e., how electrons are redistributed between adsorbate and adsorbent, which is the essence of chemisorption. Metals can generally act as either Lewis acid or base, since their HOMO and LUMO have essentially the same energy. Molecules with $\pi$-bonds can donate electrons to a metal surface (Lewis acid).[38] In metal oxides (and sulfides), the smaller the ionic component in the metal−oxygen bond, the more acidic the surface ($SiO_2$), and vice versa (CaO). Anions act as Lewis bases, cations act as Lewis acids. The smaller the cation and the higher its charge, the more acidic the surface is likely to be.[39]

### 2.2. Chemical Stability of a Molecule on a Specific Surface

An important requirement is that the candidate SMI should form a stable product on the NGS. All atomically precise deposition and etching methods have a window of deposition parameters, so the selection of an SMI candidate must satisfy these constraints. The temperature window is particularly important, and the preliminary down-selection must consider thermal stability of SMIs within the targeted temperature window of the deposition process. The thermal stability must be evaluated on specific surfaces that need to be protected. There is a tremendous amount of literature available describing surface chemistry of molecules that can be used as SMI on a variety of surfaces,[40] and this criterion can easily be tested experimentally.

Figure 3 shows the thermal stability window of Hacac, tfacH (1,1,1-trifluoroacetylacetone) and HfacH (hexafluoroacetylacetone) on different surfaces. From this example, it can be derived that the stability of chemisorbed species strongly depends on the type of $\beta$-diketone as well as on the surface to which it is bonded. The temperature window of a targeted ASD process must overlap with that of the SMI on the specific surface. The general trend suggests that nonfluorinated Hacac is more stable on oxides than the fluorinated counterparts. Based on this conclusion, a set of dosing conditions could be derived for a target combination of GS and NGS. It should also

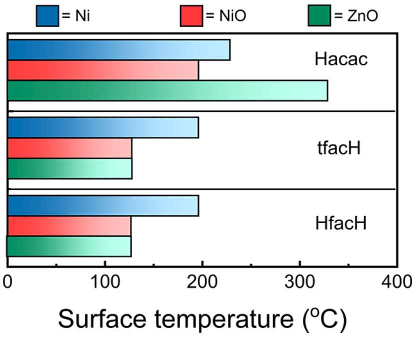


**Figure 3.** Temperature window of Hacac, tfacH, and HfacH on different metal and oxides surfaces. [Data taken from refs 42, 46, and 48.]

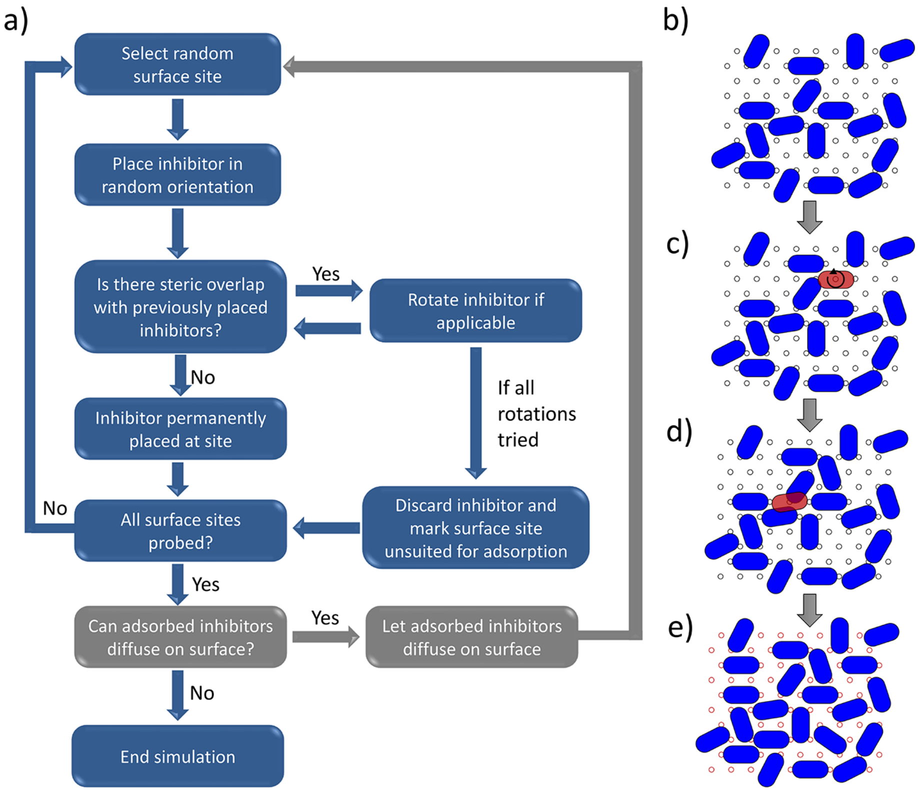


**Figure 4.** Random sequential adsorption (RSA) simulation procedure for studying inhibitor adsorption. (a) Simulation flow scheme. (b)−(e) Illustrations of the surface during different stages of the RSA simulation from low coverage (b) to saturation (e). [Reproduced with permission from ref 25. Copyright 2022, AIP Publishing.]

be noted that the surface chemistry of β-diketones is quite complex and multiple reaction pathways can coexist ranging from etching reactions and partial decomposition up to marked decomposition to form ketene-like structures.[41−47]

When choosing an SMI based on thermal stability, it is important to consider the entire process. For example, the catalytic activity of a surface in conjunction with the choice of coreactant can play substantial roles in determining whether that surface will be blocked or not. An illustration of this point is the Ru surface when $O_2$ is used as a coreactant. Despite the fact that many SMIs could be chosen based on their thermal stability on this material, its catalytic activity toward $O_2$ dissociation produces highly reactive O radicals that can combust any carbonaceous SMIs that might be bonded at this surface, even if they are thermally stable by themselves.[27]

## 2.3. Volatility

For practical reasons, SMIs ideally should have low toxicity, be inexpensive, and have high chemical stability so that they are easy to handle and store. In a perfect analogy with ALD/CVD precursors, in order to be efficiently transported in a gas phase to the surfaces where reactions should happen, the SMI candidates have sufficiently high vapor pressure. This criterion overlaps drastically with the stability criterion outlined above. Fluorinated hydrocarbons are generally more volatile than their nonfluorinated analogues. For example, the heat of vaporization ($\Delta H$) of HfacH is 27.05 (with a boiling point of $T_{\text{boil}}$ = 343 K), compared to 41.78 kJ/mol for Hacac ($T_{\text{boil}}$ = 411 K) and larger diketones, such as 2,2,6,6-tetramethyl-heptane-3,5-dione, are solid at room temperature.[49] This brief comparison would clearly favor the use of HfacH as a potential SMI; but the volatility criterion must be secondary to the thermal stability on a target surface. Of the three diketones, HfacH decomposes on ZnO at the lowest temperature. If this thermal limit is compatible with the deposition scheme, the choice of HfacH is obvious. For higher temperature limits, Hacac or even methyl-substituted acetylacetones must be considered.

## 2.4. Steric Hindrance, Geometry, Packing, and Precursor of Choice

The primary role of SMI is blocking the potential deposition process on a selected NGS. This entails knowing what type of reactive sites are involved in the ALD process and targeting them with SMI to inhibit precursor reactions. Therefore, chemical passivation and steric blocking are major factors in selecting appropriate SMIs. Chemical passivation is often ensured by alkyl groups; because of extremely low polarizability (Pauling's electronegativity for C = 2.55 and for H = 2.20) charges are equally distributed making alkyl groups less prone to attract and subsequently react with ALD precursors (Lewis acids such as TMA, $TiCl_4$) and common coreactants (Lewis bases such as $H_2O$, $NH_3$). From this consideration, it immediately follows that the presence of strong electron-withdrawing effects can increase the polar character of alkyl groups causing, for example, stronger attraction forces with precursors and thus longer residence time at the surface. This ultimately can cause "parasitic" reactions with the subsequent ALD step that lead to nucleation and thus loss of selectivity. Steric hindrance, geometry, and packing should be considered together with the precursor of choice and the specific NGS, since these properties are all related.

The specific properties of the NGS provide indications about the density, distribution, and type of reactive sites. The ideal SMI should be capable of screening off all the reactive

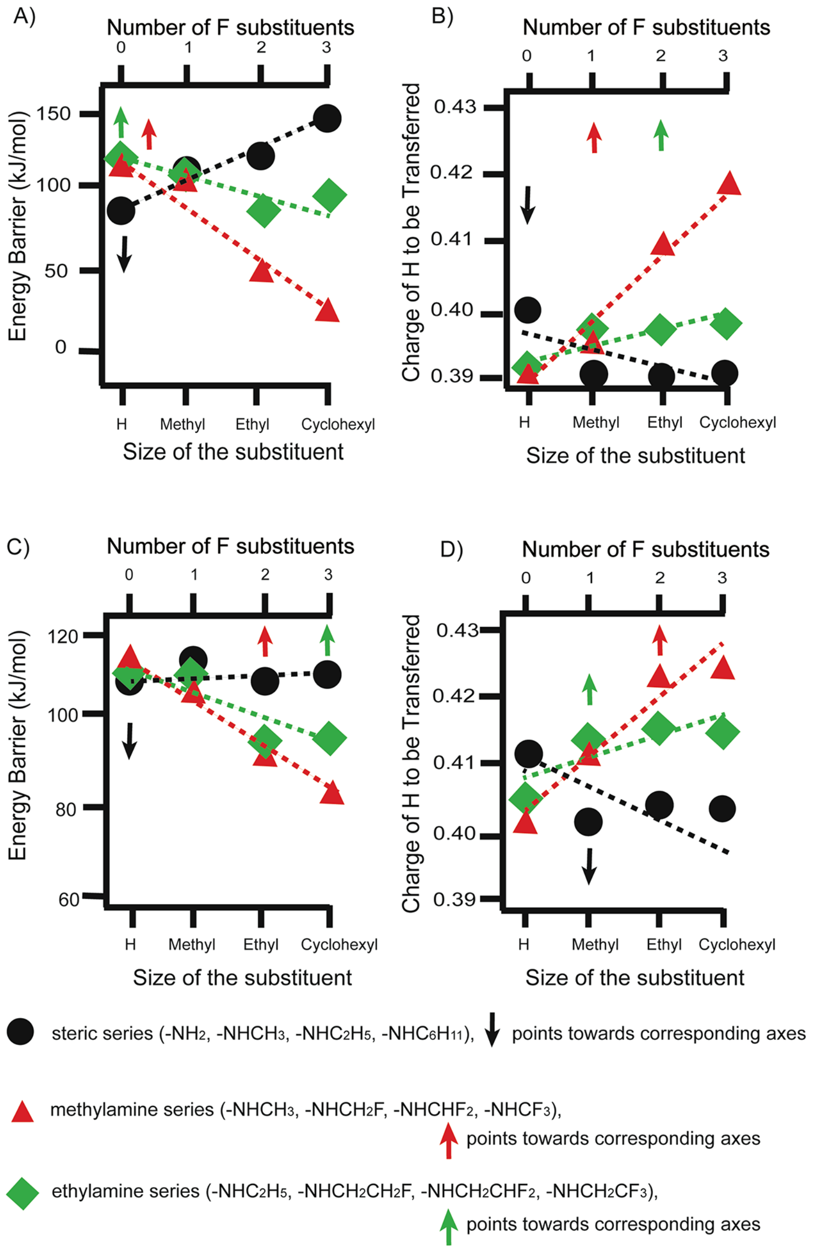


**Figure 5.** Summary plots of energy barriers for (A) TDMAT and (C) TMA abstracting hydrogen from surface amine groups and the charges on the hydrogen atoms to be abstracted from the surface amines for (B) TDMAT and (D) TMA, using natural bond orbital (NBO) analysis. Black circles denote the steric series; green diamonds represent the electronic series based on ethylamine; red triangle represents the electronic series based on methylamine. The dashed lines are provided to guide the eye without a specific fit. [Reproduced with permission from ref 2. Copyright 2015, American Chemical Society.]

sites; therefore, the size and geometrical arrangement of the chemisorbed SMI must be related to the distance between reactive sites of the given NGS. Furthermore, the gaps (open spaces) between chemisorbed SMIs must be smaller than the incoming precursor, so that the latter may not be able to reach the surface and subsequently react.[50] It suddenly becomes clear that finding the best SMI is an extremely challenging task, because one (i) must know the surface structure; (ii) must assume a single chemistry and no long-range adsorption effects; and (iii) must decide on the uniformity of surface adsorption sites, which is often not the case for −OH groups that can form multiple structures on surfaces including isolated, hydrogen-bonded, and gem-diols. Luckily, the random sequential adsorption of SMIs presents an excellent starting point, as described by Li et al. and summarized in Figure 4.[25] This work also describes how this initial important model can be refined to include the distribution of surface reactive sites blocked by the steric factors of the SMI candidates. As a specific example of the interplay of the steric factors and surface distribution of underlying reactive sites, a maximum geometrical coverage of 4.7 $nm^{-2}$ and 4.3 $nm^{-2}$ was calculated for phosphonic acid in a monodentate binding on boehmite $\gamma$-AlOOH (010) and bayerite $\beta$-$Al(OH)_3$ (001), respectively, by Lauschtinetz et al., using density functional theory (DFT).[51] Here, the coverage of phosphonic acids has been calculated on different $Al_2O_3$ structures. Overall, different hydroxyl arrangements can result in different gaps (open spaces) between phosphonic acid molecules. Therefore the availability of potential reactive sites differ dramatically, highlighting the importance of knowing how reactive sites are distributed.

The next point to consider for attempting to match a specific surface with an appropriate SMI is the nature of the resulting chemical bonding and, thus, the geometric structure of the adduct produced by SMI. The exact structures of many adsorbed species have been investigated in great detail on a variety of surfaces. For example, possible structures of carboxylic acids, ketones, diketones, alcohols, and many other compounds have been described on a variety of transition-metal oxide surfaces, both under vacuum and ambient conditions.[36] A very detailed review of oxide surface chemistry was compiled in a special issue of *Chemical Reviews* with an introduction by C. T. Campbell and J. Sauer.[52] Two points must be taken into consideration when using this approach to identify a good SMI. First, the size and structure of the adsorbed molecule definitely give an idea about the geometric consideration for accessibility of the surface by a deposition precursor molecule; however, the dynamics of formation of the attached surface adduct may also be important, effectively changing the footprint of the masked surface. Second, various surface attachment sites, and more precisely, their combinations, must be considered simultaneously.

To illustrate the first issue, we could compare the role of different halogens on blocking reactive sites presented by dangling bonds on silicon surfaces. In the work of Butera's group, they demonstrated that a perfect Si(100) surface terminated with I atoms is more stable than the same surface terminated by Br or Cl, specifically toward oxidation or metal deposition.[53] Although the electronic effects are most definitely pronounced, it was suggested that a steric effect may be sufficient to understand this sequence. On the other hand, if a surface is modified by a relatively large attached molecule, such as 2,2,6,6-tetramethyl-heptane-3,5-dione, for example, the rotation of the methyl and *t*-butyl groups may make the footprint of such a blocker much larger than that suggested by a static picture. At the same time, the intermolecular interactions must be taken into account, since, for organic layers with high coverages, this may lead to substantial steric hindrance between neighboring SMI molecules and, thus, less effective blocking than would be expected.

The steric effect is often strongly coupled with the electronic effect of the SMI's blocking groups. Figure 5 compares these effects for a computational investigation of tetrakisdimethylaminotitanium (TDMAT) and trimethylaluminum (TMA) reaction with different functionalized Si(100) surfaces represented by cluster models and SMIs represented by modified amino groups (−NHR, where R = H, methyl, ethyl, and cyclohexyl). Being rather bulky itself, TDMAT shows great sensitivity to the size of the surface alkyl substituent, as summarized by black circles in Figure 5A. However, the structure of the surface amino-groups does not change the reactivity of TMA, which can clearly find the appropriate geometry, regardless of the surface substituent, as shown by black circles in Figure 5C. At the same time, if a selected number of H atoms in $\alpha$ or $\beta$ positions are replaced with F atoms, the surface reactivity is changed dramatically and even reversed in the case of TDMAT (green diamonds and red triangles in Figure 5A and 5C) despite the fact that this substitution does not noticeably change the bulkiness of surface protective groups. Thus, a different measure has to be involved to evaluate the role of electronic factors, as is summarized in the same Figure 5 in panels B and D using the charge of surface hydrogen atom to be transferred to an amino group in the attachment reaction or a measure of surface acidity/basicity. A similar approach can be taken in matching the SMI with a specific substrate, as was illustrated by Li et al. in evaluating tantalum oxide deposition on acidic ($MnO_2$, $SiO_2$, $Ta_2O_5$) and basic ($Al_2O_3$ and $HfO_2$) oxide surfaces.[54]

Nevertheless, for any series of chemically similar or homologously different substituents in SMIs, the role of steric effects clearly offers a great handle for using bulkier precursors to improve the selectivity, provided that changing the precursor does not affect all of the other constraints.

Furthermore, $Al_2O_3$ often has geminal OH groups that would favor bidentate binding of boronic functional groups, whereas on $TiO_2$, the monodentate attachment is predominant. In a liquid-phase modification, this was shown to be the case for respective nanomaterials,[55] and similar ideas must be considered for gas-phase SMIs. For example, it has been demonstrated that dimethylamino-trimethylsilane (DMA-TMS) can very efficiently passivate hydroxyl groups on the $SiO_2$ surface.[19] Regardless of specific arrangements of hydroxyl groups on silica (individual or hydrogen-bonded), these surface functional groups are easily passivated by aminosilanes and several other compounds;[56,57] however, reactivity of DMA-TMS is clearly different with hydroxyl groups on the $TiO_2$ surface. Specifically, there is a clear difference in reactivity of hydrogen-bonded and non-hydrogen-bonded hydroxyl groups on $TiO_2$ surface with DMA-TMS. In fact, this difference can be used to increase the selectivity in deposition processes on $SiO_2$ and $TiO_2$. It is important that the chemical mechanisms of passivation and deposition are considered carefully. As shown in Figure 6, the entire chemistry may be different for different materials. DMA-TMS effectively removes fluorine contaminations from Ti surface but leads to complex deposits on an oxidized ruthenium surface.

Finally, when deciding on the appropriate SMI, it is also necessary to evaluate the change of surface structure of the NGS as a function of experimental conditions needed for a specific deposition scheme. It is well-known that the type and relative amount of surface reactive groups that are present at a surface may depend on the temperature. For the case of $Al_2O_3$ and Hacac as SMI, it was found that higher deposition temperature improves the blocking of trimethylaluminum. As shown in Figure 7, this can be explained by the fact that, at high temperature, the surface concentration of vicinal hydroxyls is drastically decreased while Hacac can still chemisorb on isolated groups and prevent them from reacting with incoming TMA.

## 3. FURTHER DOWN-SELECTION: STRENGTH OF ADSORPTION, FAST ATTACHMENT KINETICS, AND NUMBER OF BINDING MODES

Once a handful of potential SMIs has been identified, down-selection criteria can include the comparison of their *relative* stability and several additional practical considerations.

For a set of SMIs with similar properties, the thermal stability on a specific surface and chemical stability, with respect to the target deposition precursors, should be considered further. The relative stability of several SMI candidates can be evaluated by their capabilities to displace alternative SMIs in a simple set of experiments, where the surface is initially saturated with one SMI and then exposed to a different one under conditions amenable for ALD. This

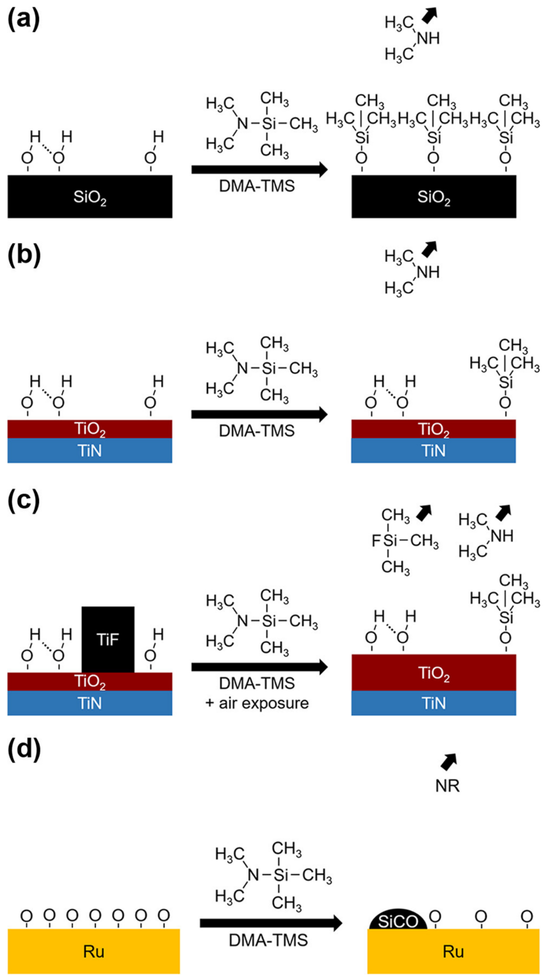


**Figure 6.** DMA-TMS surface reactions on $SiO_2$, $TiO_2$/TiN, and Ru: (a) DMA-TMS silylates $SiO_2$; (b) DMA-TMS silylates only 5% of the native $TiO_2$ on as-deposited TiN; (c) DMA-TMS cleans $TiO_2$/TiN surfaces, which display TiF post-etch residues through a surface defluoridation reaction while silylating a fraction of the surface; and (d) DMA-TMS forms SiCO islands on Ru through reaction with surface oxygen. The R group in the reaction product can include Si, O, C, and/or H. [Reproduced with permission from ref 19. Copyright 2020, American Chemical Society.]

approach was described in detail by Kung and Teplyakov for comparing the stability of ZnO powder surface exposed to ethanol, Hacac, acetic acid, and HfacH.[1] The work correlated the computationally predicted stability with the experiments following the interdisplacement in each possible combination by infrared spectroscopy, as summarized in Table 2. Of course, the displacement experiments were performed under conditions away from equilibrium, but this is what made the test more practical and relevant to the ALD work. In fact, when a combination of different SMIs may be considered, this roadmap provides a useful tool to evaluate the concentration of the SMIs reacted with a target surface if dosed sequentially or coinjected.

### Table 2. Correlation Observed between the Predicted Enthalpic Driving Force for Displacement (Difference in Surface Stability Predicted Computationally) and the Percent of Adsorbate Left on a Surface Following Displacement Process for the Four Reagents Investigated[a]

| | reagent saturating the ZnO surface before displacement (starting coverage is taken as 100%) | | | |
|---|---|---|---|---|
| displacing agent | ethanol | Hacac | acetic acid | HfacH |
| ethanol | N/A | $\frac{\sim 100\%}{77.8\ \mathrm{kJ/mol}}$ | $\frac{\sim 100\%}{116.0\ \mathrm{kJ/mol}}$ | $\frac{\sim 100\%}{154.1\ \mathrm{kJ/mol}}$ |
| Hacac | $\frac{34\% \pm 4\%}{-77.8\ \mathrm{kJ/mol}}$ | N/A | $\frac{\sim 100\%}{38.2\ \mathrm{kJ/mol}}$ | $\frac{\sim 100\%}{76.3\ \mathrm{kJ/mol}}$ |
| acetic acid | $\frac{10\% \pm 3\%}{-116.0\ \mathrm{kJ/mol}}$ | $\frac{33\% \pm 4\%}{-38.2\ \mathrm{kJ/mol}}$ | N/A | $\frac{68\% \pm 2\%}{38.1\ \mathrm{kJ/mol}}$ |
| HfacH | $\frac{\sim 0\%}{-154.1\ \mathrm{kJ/mol}}$ | $\frac{66\%}{-76.3\ \mathrm{kJ/mol}}$ | $\frac{65\% \pm 3\%}{-38.1\ \mathrm{kJ/mol}}$ | N/A |

[a] Data taken from ref 1.

In addition to forming a chemically stable bond with the NGS, the SMI should ideally react quickly and in a self-limiting manner, so that the additional SMI step does not affect the overall throughput.

The very nature of the task in hand is quite complex, meaning that simplifying the SMI selection would be generally helpful. For example, if one of the two potential SMI candidates can only bind to a surface producing one type of adduct and another candidate can undergo several different attachment pathways, the preference could be given to the simpler chemistry of the first candidate. One main reaction pathway obviously makes the processing and analysis simpler.

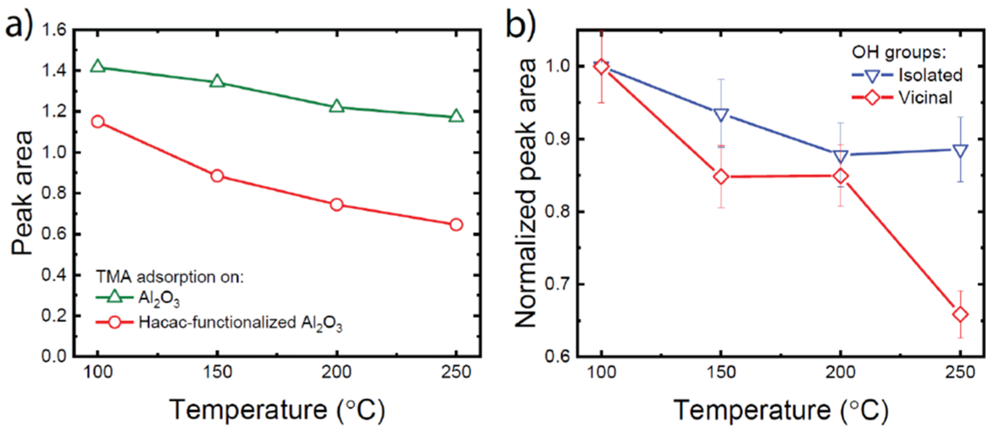
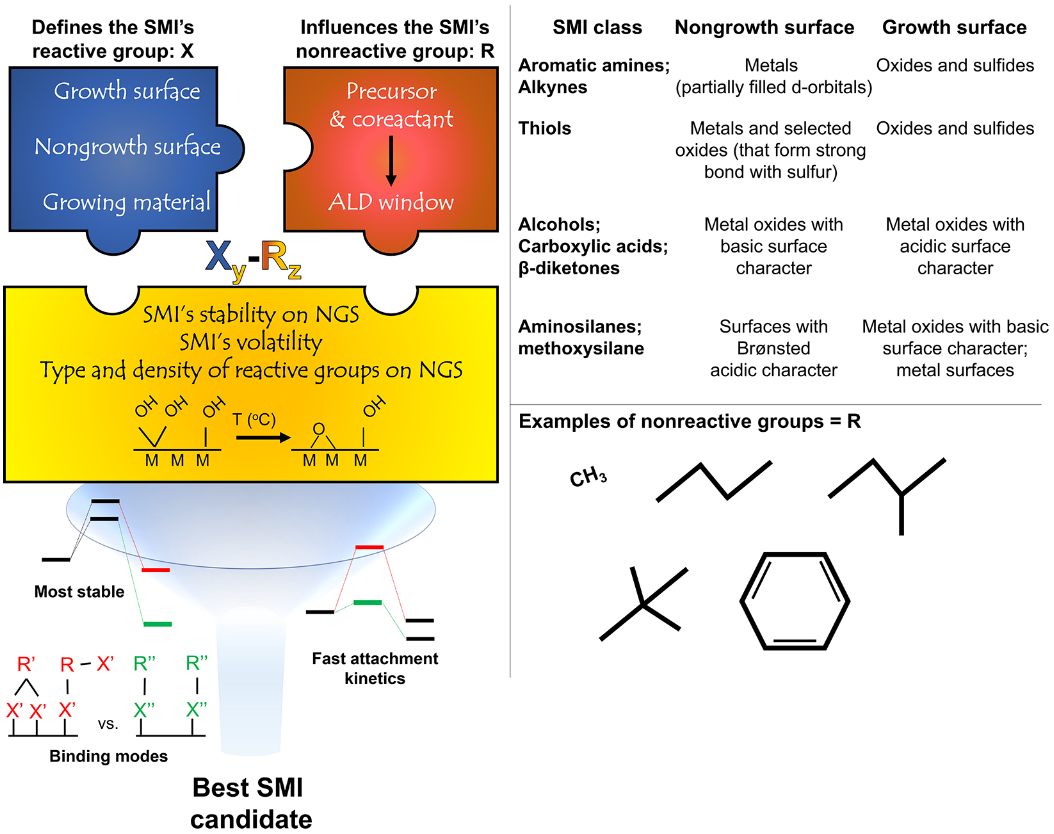


**Figure 7.** (a) TMA peak area as measured by IR spectroscopy for TMA chemisorption on clean and functionalized $Al_2O_3$. (b) IR peak area for isolated and vicinal OH groups as a function of the processing temperature. [Reproduced with permission from ref 4. Copyright 2022, American Chemical Society.]



| SMI class | Nongrowth surface | Growth surface |
|---|---|---|
| Aromatic amines;<br>Alkynes | Metals (partially filled d-orbitals) | Oxides and sulfides |
| Thiols | Metals and selected oxides (that form strong bond with sulfur) | Oxides and sulfides |
| Alcohols;<br>Carboxylic acids;<br>β-diketones | Metal oxides with basic surface character | Metal oxides with acidic surface character |
| Aminosilanes;<br>methoxysilane | Surfaces with Brønsted acidic character | Metal oxides with basic surface character; metal surfaces |

Examples of nonreactive groups = R

**Figure 8.** Conceptual summary of the SMIs selection process, together with examples of SMI classes and nongrowth and growth generalized requirements and examples of nonreactive groups for SMIs.

However, this criterion depends drastically on the nature of the surface sites to be passivated and the actual deposition chemistry. Taking the example of Hacac, two different chemisorption modes on $Al_2O_3$ have been identified, leading to monodentate versus bidentate binding configurations. The former is less stable and may be even counterproductive for precursor blocking, since the free carbonyl group can act as a reactive site for precursor adsorption.[4] On the other hand, if multiple different surface reactive sites can initiate the deposition on a NGS, and if a single SMI candidate can passivate them all with respect to the deposition precursor, this candidate gets the nod. In other words, as long as an SMI candidate chemically passivates the surface with respect to a specific deposition process, the coexistence of multiple binding modes and reaction pathways may not be an issue.

## 4. CONCLUDING REMARKS AND OUTLOOK

In this account, we outlined a strategy for selecting successful small molecule inhibitors for atomically precise surface processes based on fundamental surface chemistry considerations. We hope that by considering the steps described above, the process of finding an ideal SMI candidate can be streamlined. This summary can also help explaining previous experimental results in terms of process selectivity when comparing different deposition temperatures, SMIs, (non-) growth surfaces, etc.

Figure 8 summarizes the key aspects described in this work for selecting the ideal SMI candidate for AS-ALD.

Although the surface chemistry was not discussed in detail for each case, the examples and derived general trends already provide quite an exhaustive set of "SMI families" together with GS and NGS to generate novel processes. In particular, we encourage studies on SMI thermal stability on different NGS coupled with investigation of surface reactive sites at the NGS and the resulting precursor blocking capabilities. Such studies can provide a clear picture of the surface chemistry of SMIs from the same "family" in relation to the type of surface reactive sites and the ALD chemistry.

The specifics of SMI selection are always affected by the complexity of the overall process and will depend drastically on the specific materials and devices that are or will be needed. For example, interaction of SMIs with surfaces should be considered not only in straightforward deposition schemes, but also in supercycles, where the reactivities of GS and NGS may change substantially after the etching step. Many cases will require using several SMIs simultaneously or possibly at different stages of a process, meaning that the chemisorption chemistry as well as the displacement chemistry must be considered in concert. Finally, recent advances in ALD and ALE (atomic layer etching) require the use of complex materials that include alloys and tertiary or even quaternary (sometime van der Waals) structures, where not only selectivity but also uniformity of deposition and removal for different components of the same material must be considered. All of these complex deviations from the simplistic roadmap provided above will likely require substantial involvement of machine learning to help in down-selecting SMIs based on their surface chemistry on specific surfaces and their reactions with specific precursors.[58,59]

Finally, we would also like to point out that the logistics of this work also relies heavily on the broader work in chemical science and engineering toward understanding the ways to stimulate or slow down chemical reactions in a rational way. We hope that further inspiration can be drawn from heterogeneous catalysis and catalyst poisoning,[60] fundamental evaluations of surface acidity or basicity,[39] dynamics of coadsorption and displacement,[1] and possibly even from biological systems.[61] With this article, we hope to connect many of these approaches to area-selective deposition and also to further interconnect many of these fields.

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