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Role of Surface Termination in Atomic Layer Deposition of Silicon Nitride

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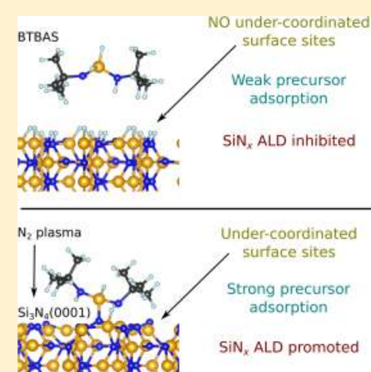
Supporting Information

ABSTRACT: There is an urgent need to deposit uniform, high-quality, conformal SiN_x thin films at a low-temperature. Conforming to these constraints, we recently developed a plasma enhanced atomic layer deposition (ALD) process with bis(tertiary-butyl-amino)silane (BTBAS) as the silicon precursor. However, deposition of high quality SiN_x thin films at reasonable growth rates occurs only when N_2 plasma is used as the coreactant; strongly reduced growth rates are observed when other coreactants like NH_3 plasma, or N_2−H_2 plasma are used. Experiments reported in this Letter reveal that NH_x- or H- containing plasmas suppress film deposition by terminating reactive surface sites with H and NH_x groups and inhibiting precursor adsorption. To understand the role of these surface groups on precursor adsorption, we carried out first-principles calculations of precursor adsorption on the β-Si_3N_4(0001) surface with different surface terminations. They show that adsorption of the precursor is strong on surfaces with undercoordinated surface sites. In contrast, on surfaces with H, NH_2 groups, or both, steric hindrance leads to weak precursor adsorption. Experimental and first-principles results together show that using an N_2 plasma to generate reactive undercoordinated surface sites allows strong adsorption of the silicon precursor and, hence, is key to successful deposition of silicon nitride by ALD.



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Continuous down-scaling of MOSFETs from the state-of-the-art 14 nm node to 10 nm node technology and beyond imposes strict requirements on the deposition of spacer materials such as silicon nitride (SiN_x). The spacer thickness should be uniform, conformal and pitch-independent. Moreover, the deposition process should use a low temperature, should have a sufficiently high throughput, and should preferably be chlorine-free for some applications.[1−4] The latter seems to be vital when using III−V channel materials in upcoming technology nodes. Currently, there exist no deposition processes for SiN_x that satisfy all the above requirements. Methods such as chemical vapor deposition (CVD) and plasma enhanced CVD (PE-CVD) either require high temperature, lead to nonconformal films, involve halide-containing chemicals in the process, or a combination of these undesirable qualities.[5,6] Also, to the best of our knowledge, no thermal atomic layer deposition (ALD)[7] process—the technique of choice to deposit highly conformal films—meets the requirements.[2] We recently developed a plasma-enhanced ALD (PE-ALD)[8,9] process[10] that meets two of the requirements—using a low temperature and being halide-free—using bis(tertiary-butyl-amino)silane (BTBAS) as the silicon precursor. However, we could deposit good quality SiN_x films with reasonable growth per cycle (GPC) only when using an N_2 plasma as the coreactant; the growth rate is strongly reduced when using other coreactants such as nitrogen−hydrogen plasma (N_2−H_2 plasma), or NH_3 plasma. Understanding the reasons for this can reveal valuable information about the reaction mechanism of SiN_x deposition during ALD. Using a combination of experiments and first-principles-based density functional theory (DFT) calculations, we show that some coreactants lead to loss of reactive undercoordinated surface sites due to termination by −H and −NH_x species. This leads to inhibited precursor adsorption on the silicon nitride surface and thereby to strongly reduced film growth. Furthermore, our experiments show that an N_2 plasma is able to regenerate these reactive sites even on a surface terminated by −H and −NH_2 groups.

The GPC from the standard process, which involves alternating pulses of precursor (A = BTBAS) and coreactant (B = N_2 plasma, N_2−H_2 plasma, or NH_3 plasma) is shown in Figure 1a. As alluded to above, we realize the highest GPC when using an N_2 plasma as the coreactant and it is strongly reduced when an N_2−H_2 plasma, or an NH_3 plasma is used (see Supporting Information for additional experimental details).

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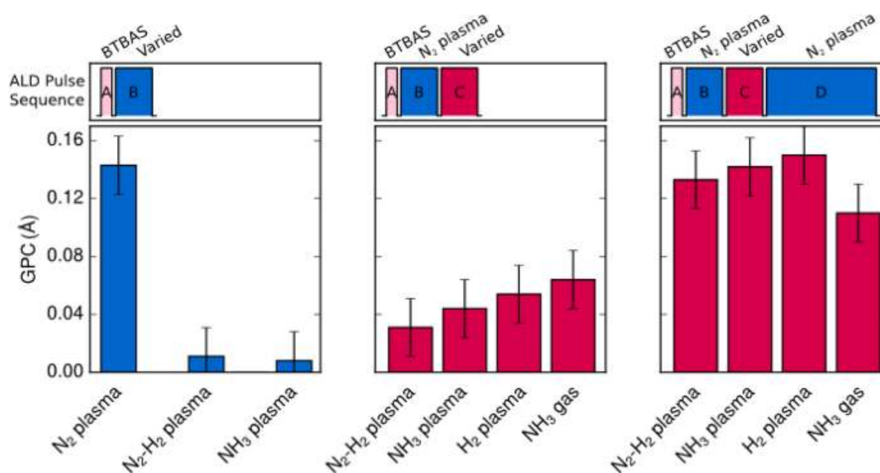

Figure 1. (a) GPC for the standard process of SiN_x ALD with BTBAS as precursor (A) and different coreactants (B = N_2 plasma, N_2−H_2 plasma, or NH_3 plasma). (b) Standard process with an additional step C (C = N_2−H_2 plasma, NH_3 plasma, H_2 plasma, or NH_3 gas) showing decreased film growth compared to the standard process with N_2 as coreactant. (c) Finally, GPC with an additional N_2 plasma step (D), after step C, showing recovery of growth due to the N_2 plasma.

Table 1. Calculated Adsorption Energies of BTBAS on Surfaces with Different Surface Terminations[a]

model	surface sites		E_{ads} (PBE) [eV] (without dispersion corrections)	E_{ads} (PBE-D3) [eV] (with dispersion corrections)	distance of Si in precursor from surface (PBE) [Å]	distance of Si in precursor from surface (PBE-D3) [Å]
M1	undercoordinated Si and N atoms	N(2c)- ; Si(3c)-	−2.86	−3.84	1.75	1.71
M2	undercoordinated Si and N atoms,	Si(3c)-; N(2c)-	−3.46	−4.45	1.74	1.73
	termination with H away from					
	adsorption site	Si(3c)-H; N(2c)-H				
M3	termination with H	N(2c)-H; Si(3c)-H	−0.02	−0.64	4.7	2.9
M4	termination with H and NH_2	N(2c)-H; Si(3c)-NH_2	−0.07	−0.72	3.1	2.4
M5	exclusive termination of N(2c) with H	N(2c)-H; Si(3c)-	−0.17	−0.83	3.4	2.9
M6	exclusive termination of Si(3c) with H	N(2c)- ; Si(3c)-H	−0.42	−3.76	4.1	1.8
M7	exclusive termination of Si(3c) with NH_2	N(2c)- ; Si(3c)-NH_2	−0.26	−0.94	2.5	2.3

[a]Distance of the Si atom in precursor from top of the surface is also listed (for M1 and M2, the distance is the Si−N bond length).

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ALD relies on the fact that in the coreactant half-cycle, the coreactant both removes ligands of the precursor that might be remaining on the surface after the precursor step and regenerates appropriate "reactive" surface sites, paving the way for a facile reaction of the precursor with the surface in the precursor half-cycle. If the coreactant fails at either of these functions, the growth per cycle will be suboptimal.

To establish if the coreactant (N_2−H_2 plasma, or NH_3 plasma) is able to regenerate the "reactive" surface, we conducted a set of experiments where we used the surface after the standard cycle of BTBAS + N_2 plasma as the starting surface. That is, we started with a surface that we know a priori has "reactive" surface sites and then introduced a third step (C). For step C, we used the coreactants that do not lead to strong growth in the standard process; that is, N_2−H_2 plasma and NH_3 plasma. A change in GPC due to step C, would signify a change in the reactive surface termination. As seen from Figure 1b, GPC is strongly reduced after the introduction of N_2−H_2 plasma, or NH_3 plasma in step C as compared to the standard process with N_2 plasma (AB cycles). From this, we can infer that precursor−surface interaction in the standard AB cycles and the ABC cycles is different. Also, because the GPC in the ABC cycles is strongly reduced, we can also infer that this new precursor−surface interaction is acting to the detriment of film growth. Furthermore, using an H_2 plasma in step C also shows strongly reduced growth, showing that H species, similar to NH_x species, inhibit growth. Finally, we observe a strong reduction in growth even when using NH_3 gas. From this, we can deduce that even the presence of reactive H, or NH_x plasma species is not necessary to make the surface unreactive: even NH_3 gas is sufficient. On the basis of these results, we propose that H, NH_x species, or both, present in an N_2−H_2 plasma, NH_3 plasma, H_2 plasma, or NH_3 gas eliminate the reactive surface sites leading to an unfavorable interaction with the precursor, thereby inhibiting its adsorption and leading to reduced film growth. One way to understand elimination of the reactive surface sites is via termination of reactive sites on the surface by H, NH_x species, or both.

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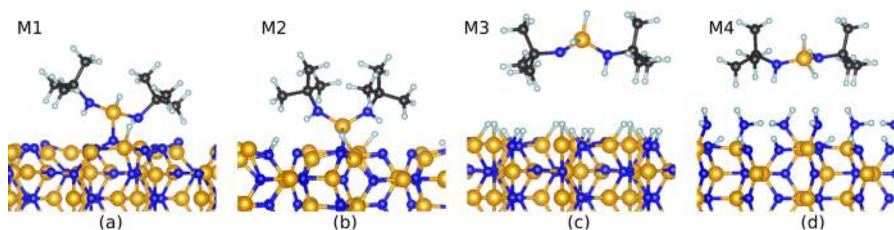

Figure 2. Optimized structures of BTBAS adsorbed on different surface termination models obtained from pure PBE calculations: (a) β-Si_3N_4(0001) with undercoordinated N(2c) and Si(3c) atoms (M1), (b) surface with undercoordinated N(2c) and Si(3c) only at the site of adsorption of the precursor (M2), (c) N(2c) and Si(3c) atoms terminated with H (M3), and (d) N(2c) and Si(3c) atoms terminated with H and NH_2, respectively (M4). BTBAS adsorbs strongly on surfaces with undercoordinated surface sites, whereas it adsorbs weakly on surfaces with H, NH_2 termination, or both. Si, N, and H are in yellow, blue, and cyan, respectively. Also see Supporting Information for optimized adsorption structures on all structural models with both PBE and PBE-D3 results.

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Now that we know reactive surface sites can be eliminated by species in the aforementioned "inhibitors" (N_2−H_2 plasma, NH_3 plasma, H_2 plasma, and NH_3 gas), we investigated if they can be regenerated by an N_2 plasma. To this effect, we introduced a fourth step (D) (Figure 1c), an N_2 plasma, immediately after the inhibitor step (C) followed by the usual precursor dose. We see that the GPC recovers to a value close to the one obtained via the standard process (Figure 1c). This establishes that a reactive surface can be regenerated by an N_2 plasma even after its elimination by species present in one of the inhibitors. Moreover, this demonstrates that precursor adsorption is dependent on the presence of reactive surface sites generated by the N_2 plasma. To summarize, from experiments, we show that H, NH_x species, or both, and even NH_3 gas can eliminate reactive surface sites created by an N_2 plasma, and that an N_2 plasma is able to regenerate the reactive surface sites.

However, the exact nature of the reactive surface sites is not clear. One common feature among all the inhibitors is the presence of H, NH_x species, or both. If we assume that undercoordinated surface sites (for example, dangling bonds, or undercoordinated N atoms) serve as reactive surface sites, H and NH_x species can bind to them resulting in their elimination (see Supporting Information on Termination of Undercoordinated β-Si_3N_4(0001) Surface with H and NH_x). It is also known that NH_3 can readily dissociate on the β-Si_3N_4(0001) surface forming N−H and Si−NH_2 bonds, eliminating reactive undercoordinated surface sites.[11] Therefore, in all the coreactants other than an N_2 plasma, we can expect passivation of undercoordinated surface sites due to the addition of H, NH_x species, or both. Linking these observations leads us to hypothesize that coreactants that eliminate reactive surface sites due to termination by H or NH_x species lead to a loss of surface reactivity. This consequently leads to weak surface−precursor interaction inhibiting adsorption of the precursor on the surface and, thereby, to reduced film growth. To test this hypothesis, we conducted first-principles calculations of precursor adsorption on the β-Si_3N_4(0001) surface with different surface terminations.

We considered six model surfaces (M1−M7) (Table 1), all derived from the β-Si_3N_4(0001) surface. Although in bulk β-Si_3N_4, the Si and N atoms coordinate with 4 N and 3 Si atoms respectively, fulfilling their valencies, the (0001) surface has undercoordinated Si and N atoms coordinated only to 3 N and 2 Si atoms, respectively. We therefore refer to the fully coordinated atoms as Si(4c) and N(3c) atoms, and the undercoordinated atoms as Si(3c) and N(2c) atoms. The model surfaces are all derived by terminating Si(3c) and N(2c) sites either with H, NH_2, or left with an undercoordinated site (see Table 1) leading to surfaces with different sites with different reactivity. This should lead to nine different models for the surface sites. However, we excluded three of these models because they are energetically unfavorable (see Supporting Information on Surface Models). In addition to the six surface termination models left, we considered a surface termination model where only the Si(3c) and N(2c) atoms directly under the precursor are undercoordinated; the rest of the atoms, away from the precursor adsorption site, were terminated with H. We did this to study how local availability (in a small area directly under the precursor) of undercoordinated sites affects precursor adsorption. We calculated adsorption energies and geometries of BTBAS both with and without dispersion (van der Waals) corrections. We used the Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional[12,13] and included dispersion interactions via Grimme's DFT-D3 method[14] (referred to as PBE-D3). However, because adsorption energies of molecules on semiconducting or insulating material surfaces have not yet been benchmarked using PBE-D3, we primarily use PBE results in our discussion; we provide the PBE-D3 results only to compare the trends. All calculations were carried out using the Vienna Ab Initio Simulation Package (VASP)[15−22] (see Supporting Information for additional computational details).

We calculate the adsorption energy as

$$E_{ads} = E_{surface+precursor} - E_{surface} - E_{precursor} \quad (1)$$

$E_{surface}$ and $E_{precursor}$ are the total energies of the isolated surface and precursor molecule respectively, and $E_{surface+precursor}$ is the total energy of the precursor adsorbed on the surface.

From E_{ads} (PBE) in Table 1, we conclude that adsorption on surfaces terminated with undercoordinated sites is much stronger than adsorption on surfaces terminated with H, NH_2, or both. On the β-Si_3N_4(0001) surface, where all of the surface Si and N atoms are undercoordinated, the adsorption is strong (M1, Figure 2 a). One of the H atoms on the precursor Si atom (Si(p)) is transferred to a surface Si(3c) atom, the Si(p) binds to a surface N(2c), and the N atoms in the precursor (N(p)) bind to two surface Si(3c) atoms. Adsorption is strong even in M2 where undercoordinated sites are only available locally; that is, only at the site of precursor adsorption and not farther away (Figure 2b). A H from Si(p) is transferred to surface N(2c) in this case too. In both of the cases, the Si−N bond lengths (Table 1) are comparable to the Si−N bond length in bulk β-Si_3N_4 (1.73−1.74 Å). However, in M2, only the Si(p) atom is bound to a surface N(2c) atom; the N(p) atoms are directed away from the surface. On both these

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surfaces, the precursor approaches close to the surface leading to a strong interaction between the undercoordinated Si(3c) and N(2c) sites on the surface and the precursor N(p) and Si(p) atoms, respectively. This facilitates strong adsorption of the precursor on the surface. As noted above, in both cases, bond breaking and new bond formation occur—a H atom from Si atom in the precursor is transferred to a Si(3c) atom on the surface—explaining the high adsorption energies. Adsorption energies of more than −2.9 eV and −3.5 eV are observed in each of the cases (Table 1).

In contrast, the adsorption of the precursor is not as strong in the case of surfaces terminated with H, or NH_2, or both. On surfaces where all of the undercoordinated sites are completely absent, the adsorption energy is low. Both in M3 (Figure 2c), where both N(2c) and Si(3c) atoms are terminated with H, and in M4 (Figure 2 d) where N(2c) is terminated with H and Si(3c) is terminated with NH_2 the adsorption is much weaker (<0.1 eV) compared to the case of adsorption on surfaces with undercoordinated surface sites (M1 and M2). The Si atom in the precursor adsorbs at a distance of 2.4 Å in M3 and further away at 2.9 Å in the case of M4. This shows that the presence of surface H, or NH_2 surface groups, or both prevents a strong interaction of the precursor with the surface.

Exclusive termination of all the undercoordinated surface N(2c) atoms with H (leaving the Si(3c) atoms undercoordinated, M5), or exclusive termination of undercoordinated surface Si(3c) atoms with H atoms (leaving the N(2c) atoms undercoordinated, M6) also prevents strong adsorption. The same also applies to the case where Si(3c) atoms are exclusively terminated with NH_2 groups (leaving the N(2c) atoms undercoordinated, M7). With pure PBE, we obtain adsorption energies of about −0.2 , −0.4, and −0.3 eV and surface H-precursor Si atom distance of 2.9, 1.8, and 2.5 Å in the three cases, respectively. This shows that notwithstanding the fact that some surface sites are undercoordinated, if access to these sites is sterically inhibited to the precursor by the presence of H , NH_2 surface groups, or both, adsorption is still weak.

We reach nearly the same conclusions as above when considering E_{ads} (PBE-D3) (Table 1). As expected, the adsorption energies are higher compared to E_{ads} (PBE-D3) due to the inclusion of dispersion corrections. The magnitude by which the precursor molecule moves closer to the surface when we include dispersion corrections is noteworthy. In M3 and M4, the precursor moves closer to the surface by about 1.8 and 0.7 Å, respectively. The influence of this closer surface bonding on the chemistry of the surface reactions is not clear and needs to be investigated further. One exception is the case of Si(3c) atoms terminated with H (M6). In this case, the H atoms in the amino group of the precursor interact strongly with N(2c) atoms on the surface. This strong interaction brings the precursor close to the surface and leads to the transfer of a H atom attached to Si(3c) to a surface N(2c) via the precursor. The strong preference of H to passivate N(2c) atoms more strongly than Si(3c) atoms explains this. For this reason, we also expect M6 to be one of the most unlikely surface models to occur under experimental conditions (also see Supporting Information on Termination of Undercoordinated β-Si_3N_4(0001) with H and NH_x). This change in bond configuration of the surface is the reason for the high adsorption energy in this case.

From the precursor adsorption energies on the above surface termination models (M1-M7), we can deduce that undercoordinated surface sites are essential for a strong precursor−surface interaction (M1 and M2). The mere presence of the undercoordinated surface sites, however, is not sufficient. Their access to the precursor should not be sterically hindered by the presence of surface H, NH_2 groups, or both (M3, M4, M5, M6, M7). Their presence hinders access to the undercoordinated sites and leads to weak precursor adsorption. Furthermore, the results from M1 and M2 indicate that availability of undercoordinated surface sites is essential only in a small radius around the site of adsorption; termination of undercoordinated sites away from the site of adsorption with H (possibly also with NH_2) does not influence adsorption. Obviously, the above conclusions are valid for the case of SiN_x ALD using the organosilicon precursor BTBAS and N_2 plasma. However, the idea that termination of film surfaces by H and NH_x species can affect precursor adsorption is general and might be applicable to other material systems as well, nitrides in particular.

Although we considered adsorption sites only in the form of undercoordinated surface sites, it is plausible that there might be other valid adsorption sites. It is hard to conjecture what these adsorption sites could be in the absence of experimental information on the nature of the silicon nitride surface after exposure to an N_2 plasma.

Our present work on the role of surface termination on surface−precursor interaction and its effect on SiN_x film growth enhances recent understanding from DFT calculations. In the study of thermal ALD of SiN_x with organosilicon precursors, BTBAS and BDEAS, with NH_3 as the coreactant, it was found that due to kinetic, thermodynamic reasons, or both, film deposition can happen only at high temperatures.[11] As we suggest in this Letter, strong adsorption of the precursor on undercoordinated surface sites (not considered in ref 2) could be a requirement for SiN_x ALD at low temperatures (also demonstrated in the experiments reported here). In another first-principles work using cluster models of β-Si_3N_4, it was suggested that the sluggishness in reactivity during thermal ALD of SiN_x using a variety of precursors and NH_3 can be attributed primarily to the rigid orientation of lone pairs on the NH_2 groups on the surface. This leads to less favorable steric interactions of precursor molecules with NH_2 terminated surfaces than with analogous OH terminated surfaces that occur on oxide surfaces.[2] Our calculations agree with the above assessment of precursor−surface interactions on the NH_2 terminated surface but also show on what surfaces precursor−surface interactions can be favorable: on surfaces with undercoordinated surface sites.

In conclusion, from a combination of experiments and first-principles calculations, we have shown that surface termination of SiN_x strongly affects precursor adsorption. From experiments, we have shown that H, or NH_x species, or both in an N_2−H_2 plasma, NH_3 plasma, H_2 plasma, or NH_3 gas leads to unfavorable precursor−surface interaction leading to strongly reduced growth; however, an N_2 plasma recovers this reduction in film growth. From first-principles calculations, we showed that surfaces terminated with H, NH_2 groups, or both lead to a weak precursor−surface interaction, whereas surfaces with undercoordinated surface sites whose access is not sterically hindered by surface H, NH_2 groups, or both lead to strong precursor−surface interaction. Control of surface termination by H and NH_x species can therefore play an important role in obtaining high quality silicon nitride films. As has been demonstrated by this work, even when plasmas are used as

coreactants, careful selection of the coreactant is key for ALD of silicon nitride.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01596.

Additional experimental and computational details, information on surface models used, and optimized structures of the precursor on all surface models considered (for PBE and PBE-D3) are available. (PDF)

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Notes

The authors declare no competing financial interest.

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