Impact of Aminosilane Precursor Structure on Silicon Oxides by Atomic Layer Deposition

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While Atomic Layer Deposition (ALD) has been in development for several decades,[1] only recently it has begun to be employed in microelectronics manufacturing technology due to the increasing dimensional control required for current and next generation integrated devices.[2,3] Atomic layer deposition of silicon oxide is now being used for various applications requiring silicon oxide films with high conformality, high uniformity, precise control of thickness and composition. In ALD processes the precursor structure plays a large role in the deposition process and film performance. A wide variety of molecular structures have been assessed ranging from chlorosilanes[4,5] and alkoxysilanes[6] to aminosilanes[7,8] and alkylaminosilanes[9]. Aminosilanes provide breadth of structural variations and may be more desirable than chlorosilanes from safety and operability perspectives. Herein we provide a comparison of three structural variants of aminosilanes: BTBAS (bis(tertiarybutylamino)silane), BDEAS (bis(diethylamino)silane), and TDMAS (tris(dimethylamino)silane). Experimental data and computational modeling analyses are combined to describe why BTBAS provides the most breadth of applicability of these precursors for ALD oxide processes.

Previous studies have shown TDMAS to be a relatively effective precursor for the deposition of silicon oxide to temperatures as low as 160ºC.[7,8,9] FT-IR adsorption studies by Kinoshita *et al.*[15] indicated surface adsorption of TDMAS on hydroxylated Si (100) surfaces even at room temperature. In this study the deposition performance of the indicated precursors is compared at essentially identical conditions using ozone as the oxidant. In general, ALD-type behavior was not observed for any of the precursors tested until deposition temperatures of 300ºC, which was the common ALD initiation point for all three precursors.

ALD Results

The depositions were performed on a laboratory scale ALD processing tool at temperatures ranging from 250°C to 575°C for either 500 or 1,000 process cycles with ozone as the oxygen source gas. Precursor was introduced by vapor draw from vessels held slightly above ambient temperature: BTBAS vessel T = 55ºC, BDEAS vessel T = 60ºC, and TDMAS vessel T = 50ºC in order to adjust for slight variations in vapor pressure and ensure consistent precursor introduction to the reaction chamber. The resultant SiO$_2$ films were characterized for deposition rate, refractive index, and % non-uniformity using spectroscopic ellipsometry. Compositional analysis was performed by dynamic secondary ion mass spectrometry (D-SIMS) by Evans Analytical Group.

The refractive index was determined by fitting the ellipsometry data from the film to a pre-set physical model (e.g., the Lorentz Oscillator model). The percentage non-uniformity quoted was obtained from a 9-point map using the standard equation: % non-uniformity = ((max – min)/(2* mean))*100.

The ALD oxide deposition performance for BTBAS using various precursor pulse times is shown in Fig. 1, where the ozone pulse was kept constant at 2 seconds and purge times were optimized for excess precursor removal and maximum adsorption coverage. A deposition rate independent of temperature is observed for the range from 300 to ~ 525ºC. For precursor pulse times ranging from 0.5 s to 3.0 s a relatively mild dependence on pulse time was observed, with the 3 s pulse showing only ~ 10% increase in deposition thickness per cycle versus a 0.5 s pulse.

For comparison of precursor efficiencies shown in Fig. 2, a constant pulse time of 2.0 s was used to further ensure each cycle was achieving saturation by the precursor. From Fig. 2 we observe a distinct difference in the deposition performance of TDMAS relative to BTBAS and BDEAS, the former achieving ~ 40% lower deposition rate relative to the latter. Kimayama *et al.*[7] also demonstrated similar trends for silicon oxide ALD deposition when comparing bis(dimethylamino)silane to TDMAS. The refractive index and deposition thickness uniformity for the three precursors shown in Figs. 3 and 4 provides further evidence that the bis-aminosilanes (BTBAS and BDEAS) demonstrate superior deposition performance for an ALD process as judged by low values for deposition non-uniformity and refractive indices closely matching that for a pure SiO$_2$ matrix (1.462).

The lower refractive index values for TDMAS films are suggestive of porosity and/or compositional impurities in the matrix. The D-SIMS profiles for carbon content of the various films deposited at 400ºC (Fig. 5) indicate an order of magnitude higher carbon content for the TDMAS films, also in very close agreement with Kimayama *et al.*[7] The compilation of this information suggests relatively poor ALD performance of TDMAS for silicon oxide by ALD at the conditions tested.

In comparing the two different bis-aminosilanes relatively moderate but significant differences are observed. BTBAS provides a slightly higher deposition rate at the conditions tested as well as a slightly wider ALD temperature window. The data suggest that the structure of the BTBAS precursor is better-suited for ALD oxide depositions relative to these other precursors tested.

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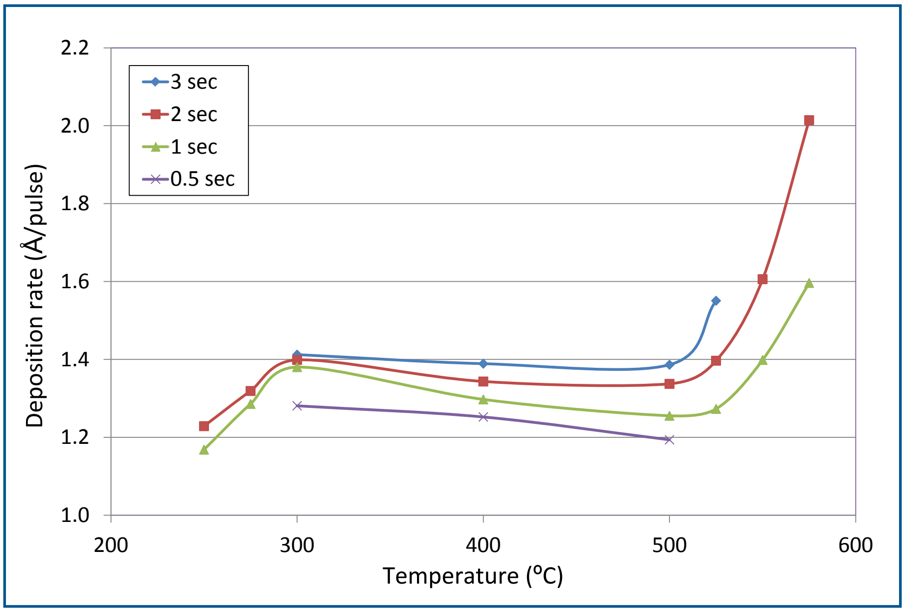

Fig. 1. *ALD deposition performance for BTBAS using 2.0 second ozone pulse.*

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Molecular Modeling

Theoretical calculations were performed using the Materials Studio software package by Accelrys.[10] A periodic surface slab model was used to mimic the hydroxylated SiO$_2$ substrate (100) surface as described in detail elsewhere.[11,12] The PW91 gradient corrected density functional[13] was used in conjunction with a double polarized numerical localized basis set and all electron approximation as implemented in the Dmol^3 module[14] in Materials Studio.

In order to better understand the results of the deposition performance, molecular modeling studies were performed using the hypothesized reaction sequence similar to that described by Kinoshita *et al*.[15] and Li *et al*.,[11] shown in Figs. 6a through 6e:

1. precursor physisorption,
2. precursor chemisorption (first intermediate state formation through amine elimination),
3. first amine desorption (formation of singly surface-bound Si species),
4. second chemisorptions step (second intermediate formation through amine elimination), and
5. second amine desorption (formation of the doubly-bound Si species; for BTBAS and BDEAS, this would result in surface SiH$_2$ species).

In the case of TDMAS an additional sequence to include a third intermediate state through the elimination of the last amine with the surface followed by the formation of a triply-bound Si moiety with a Si-H surface group could also be hypothesized.

Parts of an analogous reaction sequence was studied earlier by Li *et al*.[11,] for TDMAS and by Han *et al*.[12] for BTBAS using a plane wave density functional approach. Due to the different theoretical methodology the calculated energies of reactions are somewhat different in the current calculations, although the observed trends are unchanged for reactions which were subjects of both studies. The data here indicate that the initial physisorption step of the precursor to the hydroxylated Si surface is quite exothermic, demonstrating that there is a strong preference for all precursors to bind to the interface, in agreement with Kinoshita *et al*.[15] The chemisorption step, viewed as the first precursor-to-surface bond formation sequence, was found to be the most exothermic for BTBAS whereas this step was less exothermic for BDEAS and even endothermic for TDMAS. The differences in exothermicity may be related to subtle differences in the geometry of the post reaction complex. For the most exothermic BTBAS reaction the amine side product is not directly bound to the surface, whereas the small amines coming from the other two precursors are both surface bound and may even be viewed as still partially coordinated

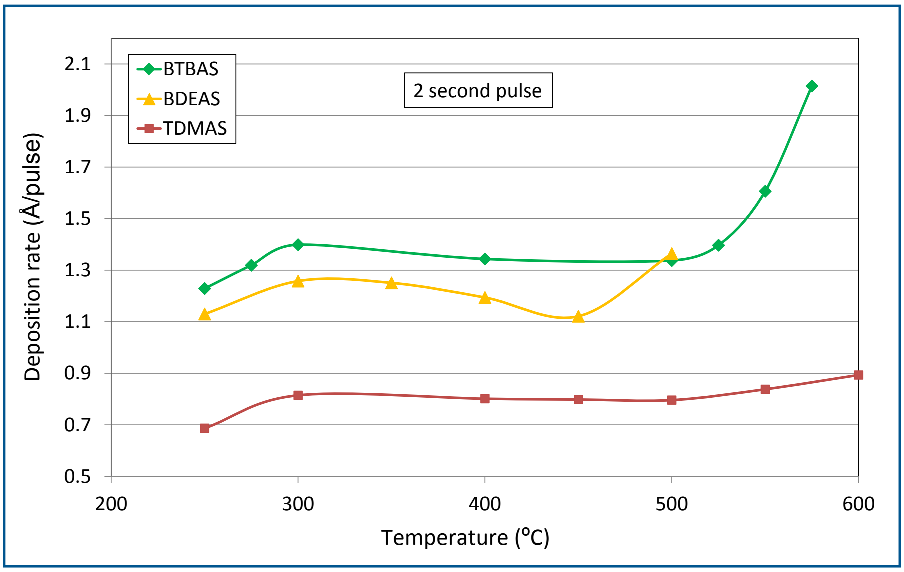

Fig. 2. *ALD deposition comparison for BTBAS, BDEAS, and TDMAS using a 2 second precursor pulse and a 2 second ozone pulse.*

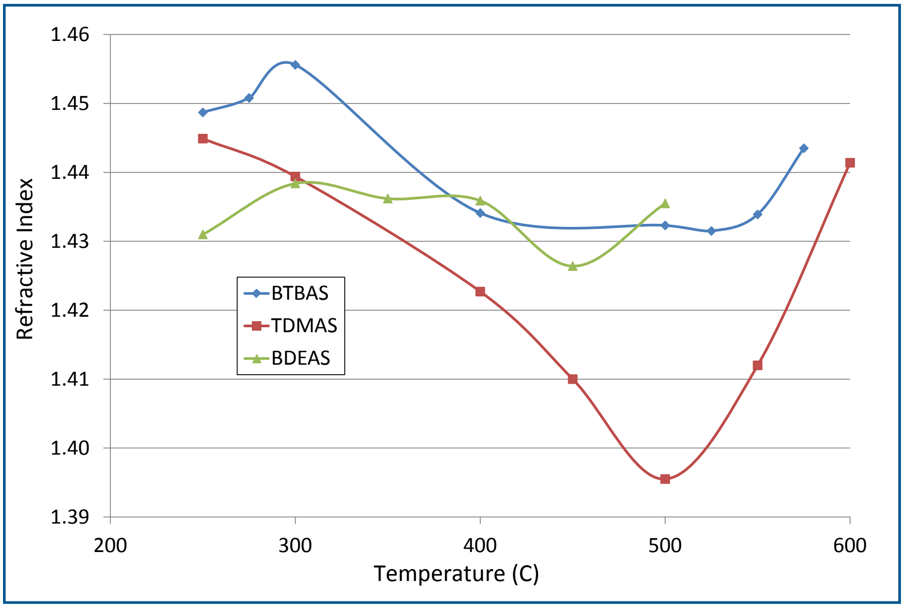

Fig. 3. *Refractive index versus temperature profiles for BTBAS, BDEAS, and TDMAS using a 2 second precursor pulse and a 2 second ozone pulse.*

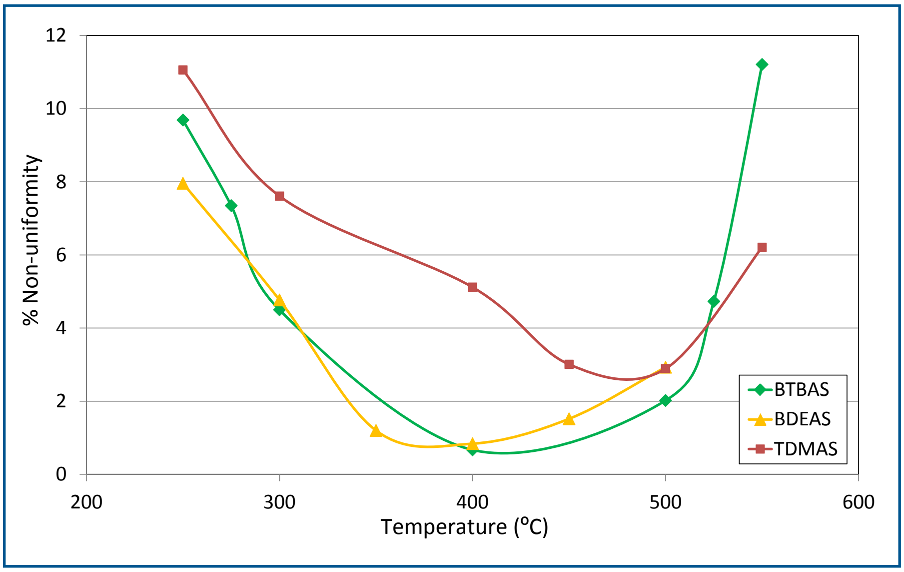

Fig. 4. *Thickness uniformity versus temperature profiles for BTBAS, BDEAS, and TDMAS using a 2 second precursor pulse and a 2 second ozone pulse.*

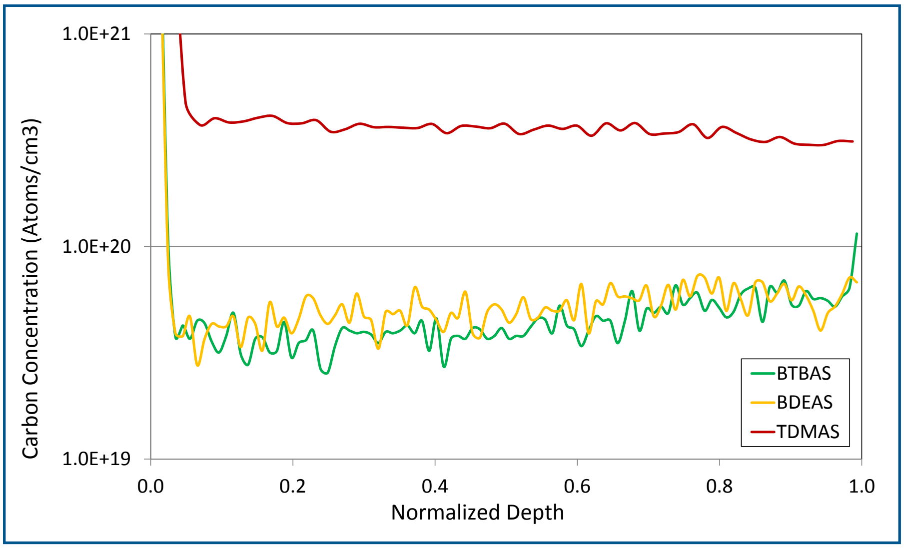

Fig. 5. *Composition depth profiles for BTBAS, BDEAS, and TDMAS using a 2 second precursor pulse and a 2.0 second ozone pulse.*

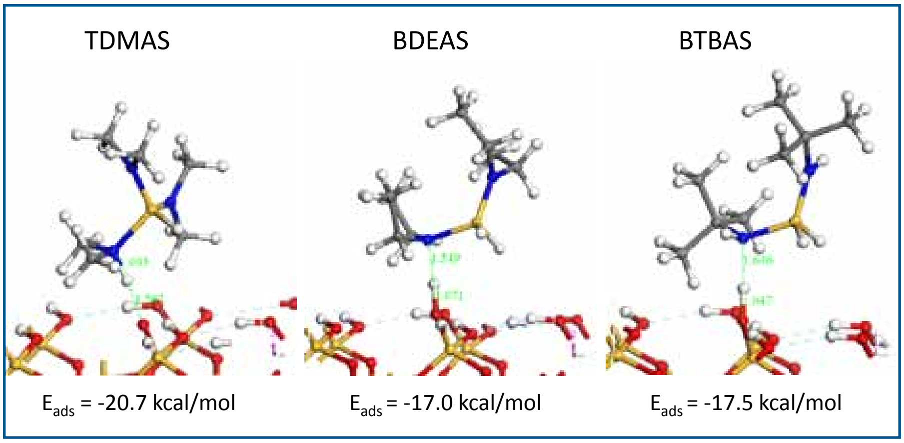

Fig. 6a. *Modeling view of precursor physisorption step comparing TDMAS, BDEAS, and BTBAS.*

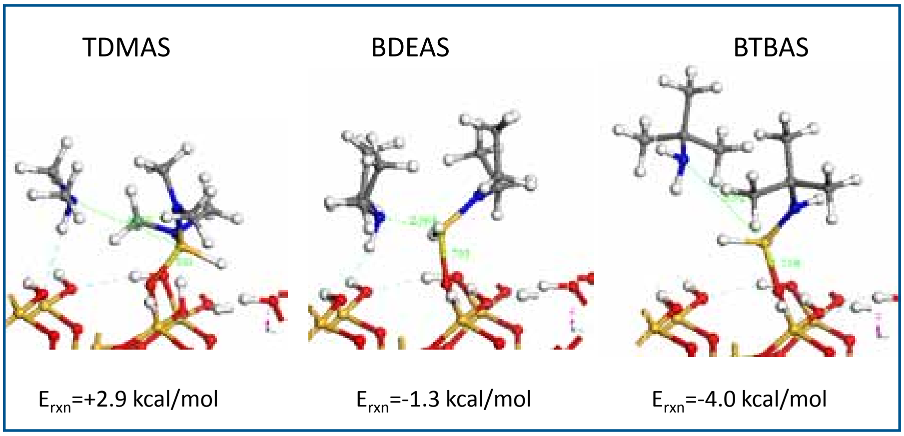

Fig. 6b. *Modeling view of precursor chemisorption step comparing TDMAS, BDEAS, and BTBAS.*

to the Si atom of the precursor.

The endothermic nature of the TDMAS reaction may at least in part be attributed to stearic effects due to the presence of the third amine substituent on the Si atom which weakens the interactions in the post reaction complex. The first amine desorption step, leading to the singly-bound-SiH_2R species for BTBAS and BDEAS and $SiHR_2$ for TDMAS, is endothermic for all precursors. It must be noted though that the extent of endothermicity is moderate for all three amines and so the reaction is expected to proceed readily at the reaction temperature used here. Through the formation of a gas phase species, this step is also entropy driven. As seen in Fig. 6d, BTBAS also has the most exothermic second amine elimination step, namely the subsequent second stable intermediate formation process en route to the double bound $=SiH_2$ surface species for both BTBAS and BDEAS, and =SiHR for TDMAS. For TDMAS there is potentially a third amine elimination/desorption sequence resulting in a triply surface bound Si-H moiety.

The overall reaction thermodynamics for all these steps resulting in terminal surface SiH_2 and Si-H species are shown in Fig. 7. The qualitative difference between TDMAS and the bis substituted precursors is clearly visible. The formation of the first post reaction complex is thermodynamically favored (exothermic) for BTBAS and BDEAS, which results in an equilibrium pushed to the right. The significant population of the surface bound product species facilitates the subsequent endothermic amine desorption step completing the first amine elimination sequence. In contrast, for TDMAS the same sequence must proceed through only a small population of the post reaction complex present at any moment making the deposition more difficult thermodynamically. Earlier calculations[11,12] for BTBAS and TDMAS showed that the amine elimination reactions have only moderate activation energies (10-20 kcal/mol) so one can expect that equilibrium is established quickly at the temperatures of interest. A similar thermodynamics based argument can be used to rationalize the larger deposition rate of BTBAS relative to BDEAS: a more exothermic first amine elimination step yields a larger population of post reaction complex on the surface which, in return, results in a larger rate for amine desorption and an overall faster first chemisorption step (assuming that the activation energy remains in the same regime as for the other 2 precursors).

The same thermodynamic arguments also carry over for the second chemisorption step: the exothermicity of reaction governs the surface populations of the post reaction complexes favoring BTBAS followed by BDEAS and TDMAS being the least exothermic and, consequently, the slowest to complete this step. Again, the step is not expected to be kinetically controlled due to the modest (10-20 kcal/mol activation energies found for TDMAS and BTBAS[11,12]). It also must be noted that the second amine desorption is more difficult energetically than the first one for all three precursors, probably due to the more acidic nature of the remaining silicon species.

In recent studies by Li *et al.*[11] it was demonstrated that in contrast with the removal of first and second amine substituents, the third amine removal sequence, as required for TDMAS, is kinetically very difficult. The reaction appears to have a very high activation energy (70-90 kcal/mol depending on orientation), which makes the complete removal of the amine groups from the films exceedingly challenging.

Comparison with Experimental Results

In rationalizing the experimental work based upon these modeling insights, there appears to be excellent consistency in the data. The bis-aminosilane precursors both appear to yield good ALD silicon oxide performance with high deposition rates and

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low carbon impurity, whereas experimentally TDMAS was never able to achieve ALD-like behavior due to the persistence of the third amine substituent. This resulted in poor ALD performance and high carbon incorporation in the final films produced from TDMAS.

Further support for the reduced deposition rates when using tris-aminosilanes can be rationalized through the surface packing density versus bis-aminosilanes. Since the subsequent reactive process step after precursor exposure involves exposure to ozone it could be argued that most residual amine functionality would be ultimately removed. Perhaps under more aggressive oxidative conditions the deposition uniformity and carbon content for TDMAS depositions would provide more ALD like behavior, comparable to that observed for the bis-aminosilanes observed in this study. However, when packing density studies are performed, a sub-monolayer surface loading is inevitable for the doubly-bound Si atoms arising from tris-aminosilanes which result in a =SiHR surface as shown in Fig. 8. The presence of the amine species, even the relatively small dimethylamine, significantly precludes full monolayer coverage in one cycle. The result is significantly reduced deposition rates for the tris-aminosilanes versus the bis-aminosilane, the latter forming essentially complete single layer SiO$_2$ thickness increase per cycle whereas the former here observed to be about half that deposition rate.

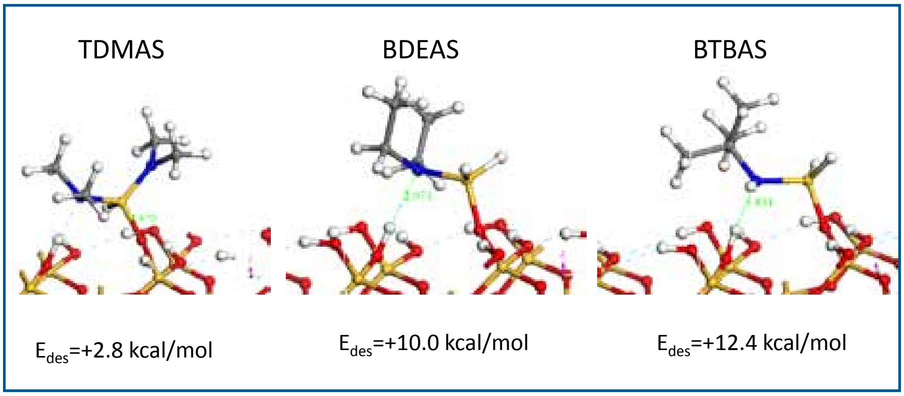

Fig. 6c. *Modeling view of first amine desorption step comparing TDMAS, BDEAS, and BTBAS.*

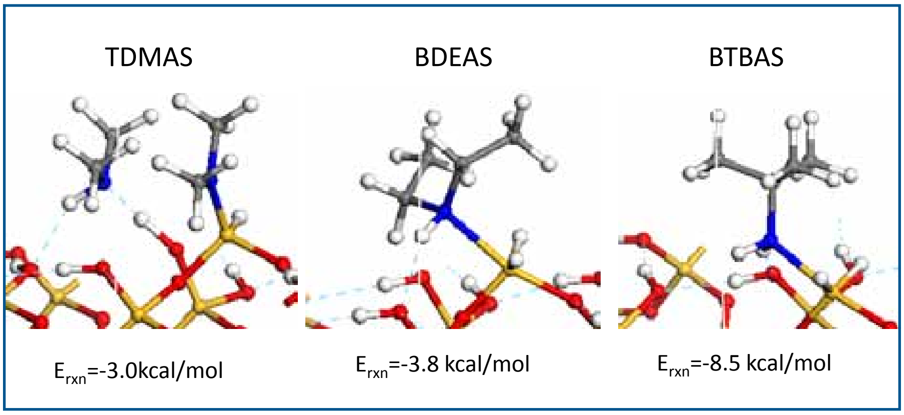

Fig. 6d. *Modeling view of formation of surface chemisorptions step comparing TDMAS, BDEAS, and BTBAS.*

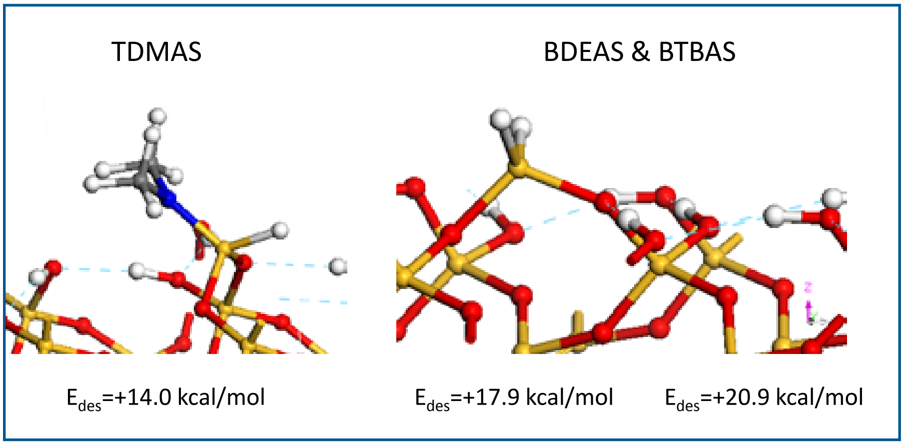

Fig. 6e. *Modeling view of second amine desorption step comparing TDMAS, BDEAS, and BTBAS.*

Conclusion

The relative deposition performance and film property data for silicon oxide ALD deposition using BTBAS, BDEAS, and TDMAS indicates that BTBAS provides the widest window of applicability as an ALD precursor, depositing films by ALD mechanism from below 300ºC to temperatures greater than 500ºC. In comparing to other bis-aminosilanes, such as BDEAS, the molecular structure of BTBAS with two tertiary-butyl amine ligands provides both reactivity at low temperatures and stability against self-reactivity to high temperatures. Further amine substitution, as in the tri-substituted TDMAS, provides a precursor with more resistance to ALD deposition mode. Molecular modeling studies further support the assertion that bis(amino)silanes provide improved performance relative to tris(amino)silanes.

About the Authors

Heather Bowen began working for Air Products in 1995, developing purification processes and scale-up activities within the Chemical Development Engineering group supporting electronic materials. She currently supervises the Air Products, Carlsbad, Applications Lab, working on LPCVD and ALD depositions and precursor development. She has a degree in biomedical engineering from the University of California, San Diego. Bowen has several issued patents in both chemical purification and thin film deposition. She may be reached at bowenhr@airproducts. com.

Kirk Cuthill started work with the Hughes Aircraft Company of Oceanside, CA in December of 1972. During the 23 years with Hughes Aircraft, Cuthill was heavily involved in wafer fabrication of integrated circuits. In November of 1995, Cuthill started work with Air Products and Chemicals in Carlsbad, CA, on the development of new silicon precursors for use in the semiconductor industry. Over the past 16 years, Cuthill has coauthored several distinct patents. He may be reached at cuthilks@airproducts.com.

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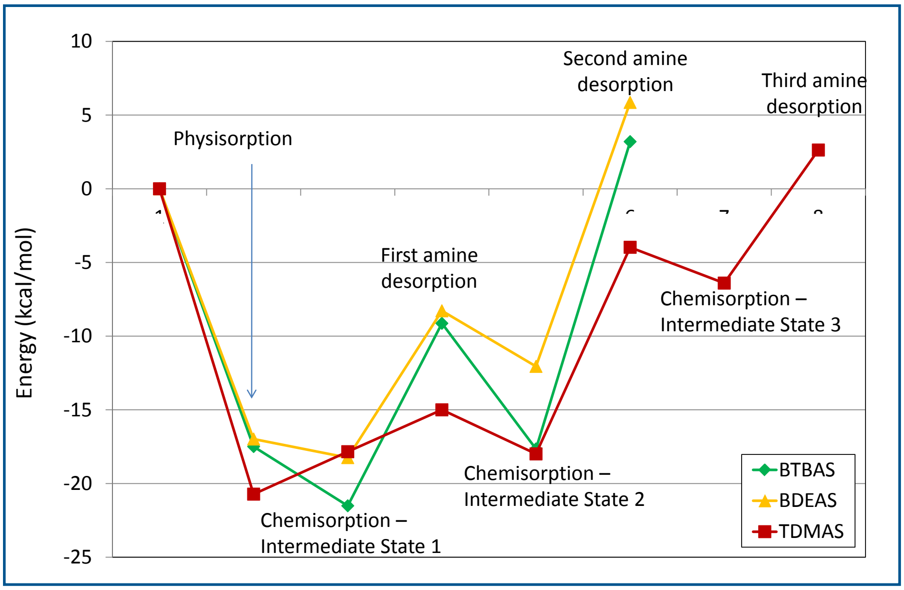

Fig. 7. *Overall thermodynamic comparison for TDMAS, BDEAS, and BTBAS.*

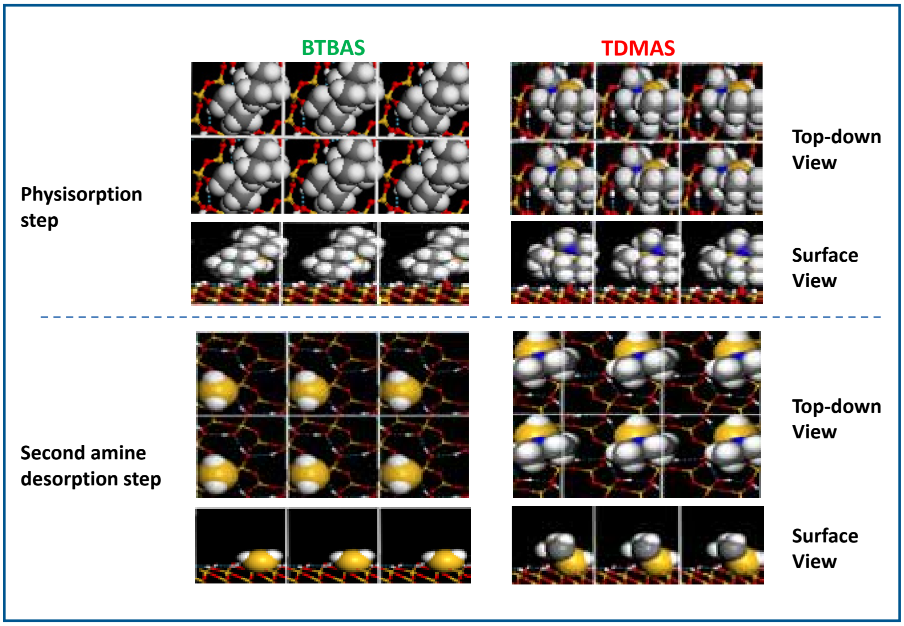

Fig. 8. *Surface packing views for BTBAS and TDMAS.*

related to the bulk and surface properties of titanium dioxide. She joined Air Products in 2010 working for the Computational Modeling Center as a Research Associate. In this role, she is responsible for the computational chemistry support globally for all Air Products businesses. She has published over 50 papers and has given numerous presentations at scientific meetings. She may be reached at derecsa@airproducts.com.

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Manchao Xiao received his PhD in organic chemistry in 1988 from Washington University in St. Louis. He was a postdoctoral fellow in Departments of Chemistry at University of Pittsburgh and University of Cincinnati (1989-1991). Dr. Xiao held a Lecturer of Polymer Chemistry position in Department of Chemistry at Shandong University (1981-1983) after he received his master's degree in polymer chemistry. Dr. Xiao joined Air Products in 2001, working as a research chemist specialized in the fileds of developing new organosilicon compounds for integrated circuit manufacture technology. He may be reached at xiaom@airproducts.com.

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