

# Electronic Structure of Two Precursors for Nanofabrication: $[(\text{CH}_3)_3\text{CN}]_2\text{W}[\text{N}(\text{CH}_3)_2]_2$ and $\text{Ti}(\text{NMe}_2)_2(\text{NEt}_2)_2$

Igor Novak\*

Charles Sturt University, P.O. Box 883, Orange NSW 2800, Australia

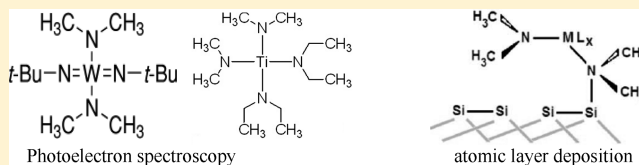
Branka Kovač\*

Physical Chemistry Department, Ruđer Bošković Institute, HR-10002 Zagreb, Croatia

Milan Jokić

Organic Chemistry and Biochemistry Department, Ruđer Bošković Institute, HR-10002 Zagreb, Croatia

**ABSTRACT:** The electronic structures of bis(*tert*-butylimino)bis(dimethylamino) tungsten and bis(*N*-ethylethanaminato)bis(*N*-methylmethanaminato) titanium heteroleptic complexes, which are precursors for atomic layer deposition of metallic nitride on surfaces, have been investigated by HeI and HeII UV photoelectron spectroscopy and DFT/OVGF calculations. We discuss the electronic structures of these two and other related  $d^0$ -type complexes in relation to the mechanism of adsorption and decomposition of metal alkylamide precursors on surfaces.



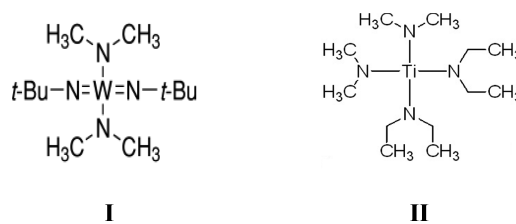
## 1. INTRODUCTION

Bis(*tert*-butylimino)bis(dimethylamino)tungsten (**I**) and bis(*N*-ethylethanaminato)bis(*N*-methylmethanaminato)titanium (**II**) complexes (Scheme 1) are two of the standard precursors used for the atomic layer deposition (ALD) by which thin films of metallic nitrides can be created on surfaces (e.g., on silicon).<sup>1,2</sup> Complex **I** is also known as bis(*tert*-butylimido)bis(dimethylamido) tungsten(VI), whereas **II** is also known as bis(diethylamido)bis(dimethylamino)titanium(IV); these alternative names are sometimes encountered in the literature.<sup>1,2</sup> Metal nitrides act as copper diffusion barriers in electronic circuits. Metal alkyl amides can be used under mild conditions (without high deposition temperatures and free of corrosive byproducts). Such mild conditions are of course ideal for the manufacture of microelectronic devices.

The ALD method is very important in the manufacturing of electronic, because it produces films with good step coverage on the nanometer scale. During the ALD process, a variety of surface reactions may take place before stable layer-by-layer growth takes over resulting in surface of uniform coverage. It is therefore important to understand the mechanisms of these surface reactions which are important in initial stages of ALD process. The reaction mechanism will be strongly influenced by the electronic structures of the precursor and the surface.

This is why we have performed the electronic structure study of these two commonly used metal alkylamide precursors (Scheme 1) by using UV photoelectron spectroscopy (UPS) and related their electronic structures to the similar complexes which have already been studied by UPS. Our two precursors

## Scheme 1. Structures of I and II



are  $d^0$  type, heteroleptic transition metal complexes. The UPS method gives an accurate description of the valence electronic structure of the free molecule (i.e., before it forms adsorbates on the surface).

## 2. EXPERIMENTAL AND COMPUTATIONAL METHODS

The samples of compounds shown below were purchased from Aldrich and used without further purification after the manipulation was carried out under an atmosphere of dry Ar in a vacuum atmosphere drybox in which the samples were transferred from a sealed ampule to the glass vial filled with Ar and then connected to the instrument inlet system. The HeI/HeII photoelectron spectra (UPS) were recorded on the Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe gas which was added to the sample flow.

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Table 1. Some Calculated (B3PW91/6-31G\*) Geometry Parameters for II<sup>a</sup>

Ti–NMe <sub>2</sub>	Ti–NEt <sub>2</sub>	Et <sub>2</sub> N–Ti–NEt <sub>2</sub>	Me <sub>2</sub> N–Ti–NMe <sub>2</sub>	nitrogen dihedral
1.9028 Å	1.9157	113.57°	108.28°	179.45° (dimethyl N) 175.47° (diethyl N)

<sup>a</sup>Nitrogen bend indicates deviation of nitrogen coordination from planarity.

The spectral resolution in HeI and HeII spectra was 30 and 70 meV, respectively when measured as fwhm of the  $3p^{-1} 2P_{3/2} Ar^+$  ← Ar ( $1S_0$ ) line. The samples were studied with the inlet probe at 60 and 70 °C, respectively. The spectra obtained were reproducible and measured at constant vapor pressure. No signs of decomposition were detected. Decomposition is usually demonstrated by the appearance of sharp intense peaks which are due to the presence of small molecules/decomposition products in the spectrometer's ionization chamber.

The quantum chemical calculations were performed with the Gaussian 09 program<sup>3</sup> and included full geometry optimization of neutral molecules using B3PW91 density functional and Stuttgart effective core potentials for all atoms as the first step.<sup>4</sup> The vibrational analysis confirmed that the resulting geometry was the true minimum (no imaginary frequencies). Subsequently, the optimized DFT geometry was used as the input into the single point calculation using the outer-valence Green's function (OVGF) method and the same basis set.<sup>5</sup> This method obviates the need for using Koopmans approximation and provides vertical ionization energies with typical deviation of 0.3–0.5 eV (depending on the size of the basis set) from the experimental values. The calculated bond lengths agree well with the gas phase electron diffraction data<sup>6</sup> (e.g., calculated and measured W=N bond lengths are consistent to within 0.04 Å). The calculated vertical ionization energies of two conformers of I with C<sub>1</sub> and C<sub>2</sub>-symmetries<sup>6</sup> are similar to within ±0.03 eV, which suggests that while our spectra probably correspond to the mixture of conformers, their electronic structures cannot be distinguished by UPS. The molecular structure of II is unknown, but the structure of related titanium amide Ti(NMe<sub>2</sub>)<sub>4</sub> has been determined by using gas phase electron diffraction and shown to be of S<sub>4</sub> symmetry.<sup>7</sup> The calculated geometry parameters in II (Table 1) can be compared with the measured parameters of Ti(NMe<sub>2</sub>)<sub>4</sub> where Ti–N is 1.917 Å, N–Ti–N angle is 114.2°, and nitrogen has planar coordination.<sup>7</sup>

### 3. RESULTS AND DISCUSSION

The HeI and HeII photoelectron spectra of I and II are shown in Figures 1 and 2. The spectral assignments are summarized in Table 2 and are based on OVGF calculations, HeI/HeII intensity variations, and comparison with UPS of related molecules and complexes.<sup>8–14</sup> The related molecules used for comparison with the ligands in I and II are organonitrogen compounds where the metal atom has been replaced by the methyl group (Table 2). The assignments are also supported by changes in relative band intensities on going from HeI to HeII radiation. The calculated HeII/HeI atomic photoionization cross-section ratios for C 2p, N 2p, W 5d, and Ti 3d are 0.31, 0.45, 0.32, and 0.79, respectively.<sup>15</sup>

**Tungsten Complex (I).** The interpretation of the photoelectron spectra of I shown in Figure 1 relies on the established assignments of photoelectron spectra of similar molecules and OVGF calculations. The OVGF calculated ionization energies indicate that we can expect a total of six ionizations below 10

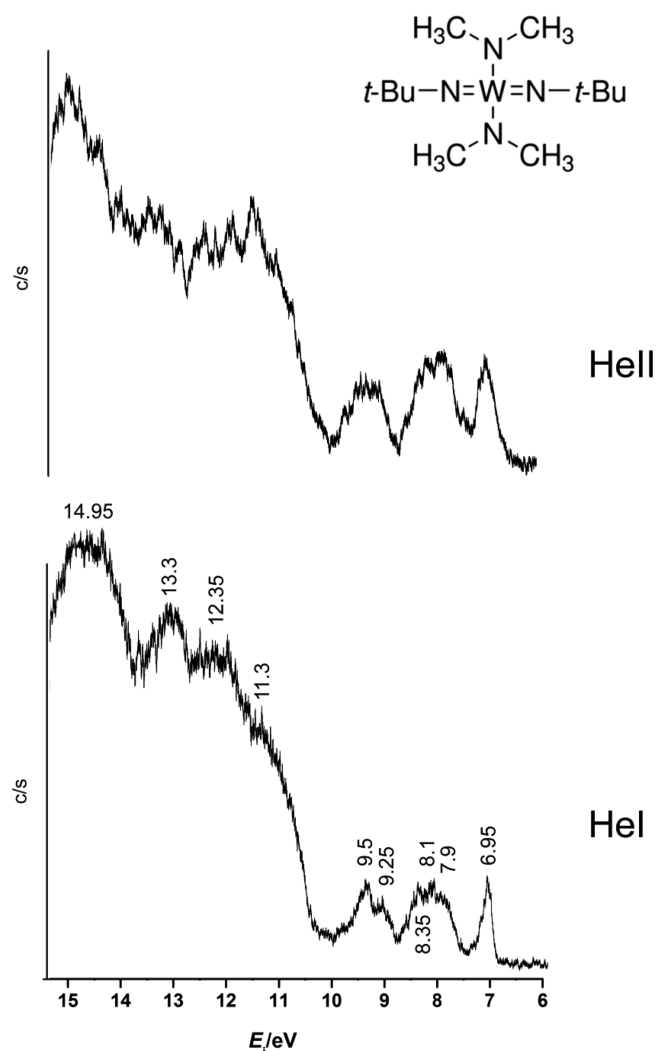


Figure 1. HeI/HeII photoelectron spectra of I.

eV, which corresponds to two imine, two amino nitrogen lone pairs as well as the nominally  $\pi_{WN}$  orbital and the orbital with predominantly W 5d character. The established assignment of the spectra of tungsten complexes containing trimethylphosphine ligands<sup>9</sup> suggests that the band at 6.95 eV in our spectra corresponds to the ionization of W 5d type orbital. This assignment also suggests that in the original assignment of W(NMe<sub>2</sub>)<sub>6</sub> the first band at 6.73 eV should be assigned to W 5d ionization rather than to the nonbonding lone pair combination as was reported previously.<sup>14</sup> The W 5d assignment had been confirmed through synchrotron radiation studies.<sup>9</sup> W 5d assignment is also consistent with the narrow width of the 6.95 eV band which indicates pronounced localization of the corresponding orbital. The assignment of partially resolved bands in the regions 7.9–8.35 eV and 9.25–9.5 eV (Figure 1) must identify bands corresponding to two amino ( $n_N^a$ ) nitrogen lone pairs, two imino ( $n_N^i$ ) nitrogen lone pairs, and  $\pi$ -orbital arising from  $p\pi \rightarrow d\pi$  bonding between

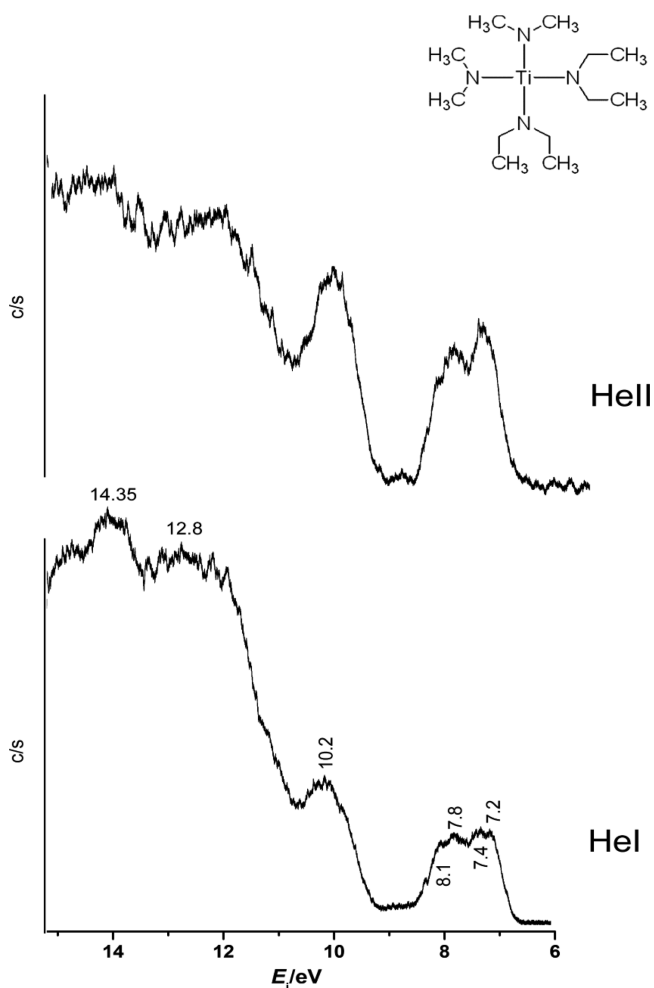


Figure 2. HeI/HeII photoelectron spectra of II.

tungsten and nitrogen ( $\pi_{WN}$ ). The nitrogen lone pair ionization energies in imine molecules: *N-tert*-butylimine and *N*-methylmethylimine are 9.25 and 9.5 eV, respectively.<sup>12,13</sup>  $\pi_{CN}$  ionizations in the same imine molecules are at 10.8 and 10.67 eV, respectively. The nitrogen lone pair in trimethylamine has an ionization energy of 8.44 eV.<sup>10</sup> On the basis of this comparison and OVGf calculations, we suggest that the partially resolved bands at 7.9–8.35 eV correspond to ionizations from three orbitals: two amine nitrogen lone pairs and one linear combination of imine nitrogen lone pairs. The bands at 9.25–9.5 eV correspond to two ionizations: one imine nitrogen lone pair combination and one  $\pi_{WN}$  ionization. This assignment is supported by changes in the relative band intensities: the band at 9.25 eV increases in relative intensity on going from HeI to HeII compared to the 9.5 eV band which decreases in intensity (Figure 1). The bands at 7.9–8.35 eV increase in relative intensity on going from HeI to HeII radiation compared to 6.95 or 9.5 eV bands. The bands which increase in intensity can be attributed to nitrogen localized orbitals, whereas those whose intensity decreases belong to orbitals with W 5d character. This interpretation is based on the atomic HeI/HeII photoionization cross-section changes for N 2p (lone pair) orbital vs W 5d orbital.<sup>15</sup>

The ionization energies of bands at 7.9–8.35 eV and 9.25–9.5 eV, which correspond to amine and imine nitrogen lone pairs, respectively, show different trends vs their precursor ligands: trimethylamine and alkylamines. The ionization energy

of amine nitrogen lone pair decreases from 8.44 eV in the trimethylamine to 7.9 and 8.1 eV in I showing only a small (0.2 eV) splitting of energies of the two amine lone pairs. The ionization energy of imine nitrogen lone pairs which are 9.25–9.5 eV in alkylamines corresponds to the two widely split (0.9 eV) bands at 8.35 and 9.25 eV in I. This different behavior can be attributed to two effects: the stabilizing  $p\pi \rightarrow d\pi$  transfer of electron density from nitrogen to vacant metal d orbitals (two-electron, two-orbital interaction) and the destabilizing repulsion between the occupied metal–nitrogen  $\pi$ -bonding orbitals (or  $\sigma$ -orbitals of the alkyl groups) and the nitrogen lone pairs (four-electron, two-orbital interaction).<sup>16</sup> The low molecular symmetry ( $C_1$  or  $C_2$  point group for the two conformers) of I places no restriction on orbital interactions/mixing.<sup>6</sup> The amine nitrogens are further away from tungsten and from each other (the W–N bonds are 197.8 pm) compared to the imine nitrogens (the W=N bonds are 177.2 pm).<sup>6</sup> Therefore, for the amine lone pairs the most important interaction is the destabilizing steric repulsion between amine lone pairs and metal–nitrogen ( $\sigma$  or  $\pi$ ) orbitals, which leads to destabilization (lowering of ionization energy compared to trimethylamine), but small energy splitting. On the other hand, the imine lone pairs experience in addition a very significant  $p\pi \rightarrow d\pi$  bonding interaction which leads to pronounced splitting of their ionization energies as was deduced from UPS.

**Titanium Complex (II).** The photoelectron spectra of II comprise two groups of partially resolved bands corresponding to four ionizations each (Figure 2). The group at 7.2–8.1 eV can be assigned to ionizations from four nitrogen lone pair orbitals, whereas the group at 10.2 eV can be assigned to four  $\sigma$  Ti–N bonding orbitals (Table 2). This interpretation is consistent with the results of OVGf calculations and with the nitrogen lone pair ionization energies in trimethylamine (8.44 eV) and *N,N*-diethylmethylamine (8.32 eV). However, nitrogen lone pairs in II interact with Ti 3d orbitals as is evident from the 0.73 eV decrease of the average nitrogen lone pair ionization energy in II compared to the average lone pair energy of the two alkylamines. The unresolved group of bands at 10.2 eV can be assigned to four ionizations from Ti–N  $\sigma$ -bonding orbitals by comparison with the spectra of related molecules and OVGf calculations (Table 2). The complex II is heteroleptic and we can identify its nitrogen lone pairs as belonging to diethylamino or dimethylamino groups by comparison with the nitrogen lone pair regions in the spectra of  $Ti(NEt_2)_4$  and  $Ti(NMe_2)_4$  complexes.<sup>14</sup> The nitrogen lone pair region in  $Ti(NEt_2)_4$  spans 6.83–7.75 eV and in  $Ti(NMe_2)_4$  7.13–8.0 eV. The bands at 7.2–7.4 eV in II can therefore be assigned to the diethylamino and those at 7.8–8.1 eV to the dimethylamino group. The most interesting question concerns the extent of  $p\pi \rightarrow d\pi$  metal–ligand interactions (i.e., the degree of involvement of Ti 3d orbitals in bonding). We could not detect the existence of such interactions in titanium(IV) *tert*-butoxide partly because the difference in photoionization cross sections between O 2p and Ti 3d orbitals is too small to induce visible changes in relative band intensities in HeI and HeII spectra<sup>17</sup> and partly because all four ligands were the same. The slightly different alkyl substitution (but with the same coordinating heteroatom) separates nitrogen lone pairs of different types of ligands on the energy scale (via predominantly inductive effect) and allows detection (using variable photon energy) of the admixture of metal orbitals. If there is no metal–nitrogen interaction, there would be no change in relative nitrogen lone pair band intensities of different

**Table 2. Experimental ( $E_i$ /eV) and Calculated (OVGF/eV) Vertical Ionization Energies, Orbital Assignments, and Relative Band Intensities in I and II and Related Molecules**

compound	band	$E_i$	OVGF	assignment	relative band intensities HeI/HeII
<b>I</b>	X	6.95	6.81	W 5d	1.0/1.0
	A–C	7.9–8.35	8.14, 8.36, 8.37	$n_N^a, n_N^a, n_N^i$	2.9/3.4
	D–E	9.25, 9.5	9.22, 9.54	$n_N^i, \pi_{WN}$	2.1/1.7
<b>II</b>	X–A	7.2, 7.4	6.98, 7.27	$n_N$	1.0/1.0
	B–C	7.8, 8.1	7.46, 7.82	$n_N$	1.0/0.8
	D–E	10.2	10.01, 10.20	$\sigma_{Ti-N}$	2.0/2.3
	F–G	10.2	10.63, 10.66	$\sigma_{Ti-N}$	2.0/2.3
NMe <sub>3</sub> (ref 10)	X	8.44		$n_N$	
MeNEt <sub>2</sub> (ref 11)	X	8.32		$n_N$	
MeCH=NMe (ref 12)	X	9.5		$n_N$	
	A	10.67		$\pi_{CN}$	
H <sub>2</sub> C=N-tBu (ref 13)	X	9.25		$n_N$	
	A	10.8		$\pi_{CN}$	
W(NMe <sub>2</sub> ) <sub>6</sub> (ref 14)	X	6.73		W 5d	
	A–F	7.92		$n_N$	
	G–H	9.55, 9.95		$\sigma(W-N)$	
Ti(NMe <sub>2</sub> ) <sub>4</sub> (ref 14)	X–A	7.13, 7.36		$n_N$	
	B–C	7.75, 8.0		$n_N$	
	D	10.32		$\sigma_{Ti-N}$	
Ti(NEt <sub>2</sub> ) <sub>4</sub> (ref 14)	X–A	6.83, 7.10		$n_N$	
	B–C	7.47, 7.75		$n_N$	
	D	9.78		$\sigma_{Ti-N}$	

alkylamido ligands. This is why we have used the heteroleptic complex **II**, rather than just the homoleptic complexes Ti(NEt<sub>2</sub>)<sub>4</sub> and Ti(NMe<sub>2</sub>)<sub>4</sub>. The cross-section difference between N 2p and Ti 3d is sufficiently large, and we have indeed noticed that the relative intensities of 7.2–7.4 and 10.2 eV bands increase compared to 7.8–8.1 band on going from HeI to HeII radiation. We conclude that the bands at 7.2–7.4 and 10.2 eV correspond to ionizations from orbitals with significant Ti 3d character; they certainly have more metal character than the orbitals of the 7.8–8.1 eV bands. This can be rationalized as follows. The lone pairs pertaining to bands at 7.2–7.4 eV belong to diethylamino groups, whereas 7.8–8.1 eV bands correspond to the lone pairs of dimethylamino groups. Ethyl substituents are more electron-donating than methyl, as evidenced by the spectra of free amines and by the spectra of corresponding titanium homoleptic complexes. The electron-donating ability facilitates  $p\pi \rightarrow d\pi$  transfer of electron density from NEt<sub>2</sub> nitrogen into the vacant Ti 3d orbitals, thus increasing metal character of the NEt<sub>2</sub> nitrogen lone pairs versus NMe<sub>2</sub>. The 10.2 eV band has Ti 3d character, because it corresponds to the ionization of Ti–N  $\sigma$ -bonding orbitals. The proposed Ti–N interactions are consistent with the experimental structure of Ti(NMe<sub>2</sub>)<sub>4</sub>, which shows trigonal planar coordination sphere for nitrogen atoms.<sup>7</sup>

**Surface Adsorption Mechanism in ALD.** The electronic structures of our complexes can be related to the proposed mechanism of dissociative adsorption of precursors which generate thin metal nitride films on surfaces.<sup>2</sup> The first mechanistic step involved in ALD of our alkylamide precursors involves nucleophilic attack by the nitrogen lone pair on the electron deficient Si surface atom. This step generates the adsorbate A1 (Scheme 2). Subsequently, A1 decomposes via the scission of either M–N or N–C bonds. The former pathway leads to the intermediate M1 within a kinetically controlled regime (low activation barrier). Scission of N–C

bond represents thermodynamically controlled regime which has a higher activation barrier, but it leads to the thermodynamically more stable product C1 (Scheme 2). This mechanistic description is supported by DFT calculations and by IR spectroscopy.<sup>1,2</sup>

We suggest an explanatory scheme for this mechanism according to which relative energies of A1 and M1 states for precursors containing different metals may be related to the ionization energies of the relevant molecular orbitals in the precursor: nitrogen lone pairs and orbitals with predominantly metal d character, respectively. This is because in M1 the metal atom forms a bond to the surface, whereas in A1, the nitrogen lone pair transfers electron density to the surface, as shown previously.<sup>2</sup>

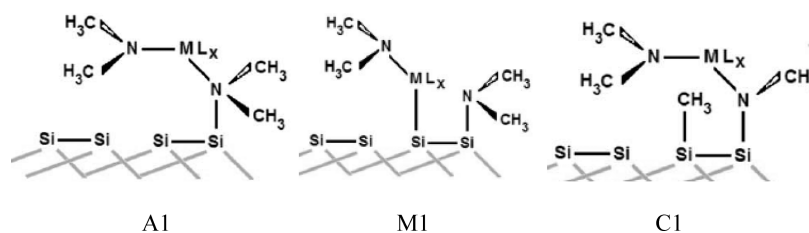
Our UPS data obtained with variable photon energy suggest that in **II** the orbitals nominally assigned to lone pairs should in fact be considered as having very significant metal character (vide supra), and therefore, we shall treat them as such (Table 3, footnote).

**Table 3. Ionization Energies of Precursors (eV) and DFT Energies of Surface States (vs Reactant Level) (kJ/mol) for Some ALD Precursors<sup>a–c</sup>**

precursor	$n_N^b$	A1 <sup>a</sup>	metal d <sup>b</sup>	M1 <sup>a</sup>
Ti(NMe <sub>2</sub> ) <sub>4</sub>	8.0	–97.8	7.13	–177.7
Zr(NMe <sub>2</sub> ) <sub>4</sub>	8.14	–120.7	7.23	–192.6
Hf(NMe <sub>2</sub> ) <sub>4</sub>	8.34	–104.3	7.50	–180.4
<b>II</b>	8.1	–70.6	6.95	–199.5

<sup>a</sup>From ref 2. <sup>b</sup>From ref 14. <sup>c</sup>Metal d orbitals span  $e + t_2$  representations, nitrogen lone pairs span  $a_1 + t_2$  in  $T_d$  coordination for precursors other than **II**, hence the UPS lone pair energies representative of “pure lone pairs” are taken to be the largest UPS ionization energies within the lone pair region in ref 14.

Scheme 2. (adopted from ref 2) Structures of the Alkylamido Intermediates A1 (left) and M1 (right) for Adsorption on Silicon Surface As Given in Ref 2. M = Metal  $L_x$  = Imine Ligand



The ionization energy of the amine lone pair is lower than the imine lone pair (in I). This implies that the lone pair electrons of amine nitrogens are held less tightly than imine nitrogens. Therefore, amine lone pairs should be more readily available for nucleophilic attack and transfer of electron density from nitrogen to the surface.<sup>2</sup> Our UPS data rationalize the reported mechanism of adsorption which indicated that the surface adsorption taking place through the amine (amido) ligand is much more important than through the imine ligand.<sup>2</sup> The predominantly metal d orbital ionization energies in I and  $\text{Ti}(\text{NMe}_2)_4$  are approximately 6.95 and 7.13 eV, respectively (Table 3). We therefore estimate that I should form a more stable surface intermediate M1 than  $\text{Ti}(\text{NMe}_2)_4$  by around 17.4 kJ/mol. This is in good agreement with the DFT prediction of 21.8 kJ/mol. The lowest ionization energies of the dimethylamino nitrogen lone pairs in I and  $\text{Ti}(\text{NMe}_2)_4$  are 8.1 and 8.0 eV, respectively. This suggests that the Ti complex should be adsorbed more strongly on the surface than the W complex (it should have a more stable A1 state) by approximately 9.6 kJ/mol, which is in only a qualitative agreement with the DFT value of 27.2 kJ/mol. What about the adsorption of other precursors for which UPS and DFT adsorption data are available? The data comparing ionization energies and energies of reaction states are summarized in Table 3. We can see that UPS and DFT data are in agreement when predicting that the  $\text{Zr}(\text{NMe}_2)_4$  should adsorb more strongly on the surface than the  $\text{Hf}(\text{NMe}_2)_4$ ; the UPS-based value from the difference in lone pair ionization energies predicts adsorption to be 19.3 kJ/mol stronger versus the DFT value, which is 16.4 kJ/mol for the A1 state. The UPS value for the M1 state is 26.05 vs DFT value of 12.2 kJ/mol. This numerical agreement is semiquantitative. However, for  $\text{Ti}(\text{NMe}_2)_4$ , the UPS and DFT predictions differ markedly. Although UPS results suggest that  $\text{Ti}(\text{NMe}_2)_4$  should adsorb more strongly than either  $\text{Zr}(\text{NMe}_2)_4$  or  $\text{Hf}(\text{NMe}_2)_4$ , this is not so according to DFT results (Table 3).

There could be several reasons for the discrepancy concerning  $\text{Ti}(\text{NMe}_2)_4$ , besides the approximations inherent in the level of DFT theory used (B3LYP/LANL2DZ). Rodriguez-Reyes and Teplyakov claim in ref 2 that this level of theory is adequate, but their arguments are based on species geometries rather than the accuracy of DFT energies (which cannot be directly compared to experimental data even if they were available). Other reasons may include the influence of additional factors (besides electronic structure) like steric interactions between precursor and surface, spatial matching of the adsorbed molecule onto the surface, or other solid state effects. Our spectra refer to free molecules while DFT results refer to the adsorbed molecules. We also note that the discrepancy of approximately 20 kJ/mol appears only in the titanium precursor. Nonetheless, we consider that our scheme can be useful at a qualitative level.

Our analysis is consistent with the proposed mechanistic pathways and with the structures and energies of some reaction intermediates shown in Scheme 2. One should ideally use appropriate bond energies when making comparisons with reaction intermediates, but because these values are difficult to measure and hence unavailable at present, we suggest the use of ionization energies instead for qualitative analysis.

It is appropriate to mention the characteristics required of a suitable ALD precursor.<sup>18</sup> They include high volatility, high thermal stability in the gas phase and on the surface, favorable chemisorption properties, and good reactivity with the surface groups. Certain metal alkylamides, for example,  $\text{W}(\text{NMe}_2)_6$ , do not possess the required characteristics.  $\text{W}(\text{NMe}_2)_6$  is known to be an extremely sterically crowded molecule with  $T_h$  symmetry.<sup>19</sup> This crowding is reflected in the experimentally determined single W–N bond lengths in I and in  $\text{W}(\text{NMe}_2)_6$ , which are 1.996 and 2.035 Å, respectively. The crowding will prevent the bonding to Si surface via the metal atom directly.<sup>2</sup>  $\text{W}(\text{NMe}_2)_6$  reacts with ROH only slowly (ROH is used to functionalize the Si surface prior and during ALD) and does not undergo the amine exchange reaction (which is involved in the ALD surface reaction mechanism).<sup>20</sup>

The metal–nitrogen bond dissociation energies for metal alkylamide species adsorbed on the silicon surface are low (approximately 24 kJ/mol for Ti–N bond).<sup>1</sup> This suggests that homoleptic, for example,  $\text{Ti}(\text{NMe}_2)_4$  (TDMAT), precursors, their heteroleptic congeners (II), and mixed alkyl species may experience scrambling (ligand exchange) on surfaces.

#### 4. CONCLUSION

Our results rationalize the theoretically proposed mechanism of adsorption and decomposition of metal alkylamides on surfaces. The ionization energies of nitrogen lone pairs in dimethylamino groups are lower (and the corresponding electrons therefore more loosely bound) than those of imino nitrogens. Thus, one can expect that the initial adsorbate complex will be formed via the bond between the amine nitrogens and surface atoms. This is in addition to the fact that bulky *tert*-butyl substituents on imine groups may hinder the access of imine nitrogens to the surface. This steric hindrance may reduce further the possibility of an imine–surface bond in the initially formed adsorbate. We have also estimated the difference in binding energies between for the intermediates of several precursors for which UPS and DFT data are available. Finally, our results indicate that UPS study of these complexes should be performed with variable photon energies in order to unravel the subtle metal–ligand intramolecular interactions.

#### AUTHOR INFORMATION

##### Corresponding Authors

\*E-mail: inovak@csu.edu.au. Tel.: 61-263657815.

\*E-mail: bkovac@irb.hr.

## Notes

The authors declare no competing financial interest.

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