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# Copper reduction and atomic layer deposition by oxidative decomposition of formate by hydrazine

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**WE HAVE USED DENSITY FUNCTIONAL THEORY (DFT) TO STUDY THE MECHANISM OF THREE STEP ATOMIC LAYER DEPOSITION (ALD) OF COPPER VIA FORMATE AND HYDRAZINE. THE TECHNIQUE HOLDS PROMISE FOR DEPOSITION OF OTHER TRANSITION METALS.**

Atomic Layer Deposition (ALD) is an innovative thin film deposition technique used today in the semiconductor industry. In principle it facilitates the deposition of materials atomic layer by atomic layer. Thus the thickness of the materials can be controlled at the sub nm level.

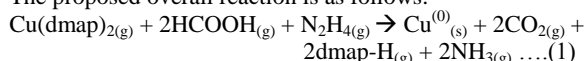
Copper is an important material in the semiconductor industry as it is used as the electrical interconnecting material within integrated circuits. For continued downscaling of electronic devices, a continuous Cu film < 2 nm thick is required as the seed layer for subsequent electrodeposition of copper interconnect. However, a problem arises as copper tends to agglomerate into discrete islands at typical deposition temperatures. This issue has received wide scale attention and is listed as one of the major problems in the semiconductor technology roadmap<sup>1</sup>.

Many attempts have been made to solve this problem by changing the precursor combination for Cu ALD. There have been reports of using Cu(hfac)<sub>2</sub> and alcohol (hfac=1,1,1,5,5,5-hexafluoro-3,5-pentanedionate)<sup>2</sup> at 300°C, CuCl and hydrogen as the reducing agent<sup>3</sup> at > 360°C and Cu(thd)<sub>2</sub> and hydrogen (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate)<sup>4</sup> at 260°C. An organometallic reagent can also be used as the reducing agent e.g. Cu(dmap)<sub>2</sub> and ZnEt<sub>2</sub> (dmap = OCHMeCH<sub>2</sub>-NMe<sub>2</sub>)<sup>5</sup> at 100°C. Cu<sup>(+1)</sup> compounds were also tested but the process appears to be closer to pulsed Chemical Vapour Deposition (CVD) rather than ALD<sup>6</sup>. Vidjayacoumar *et al.*<sup>7,8</sup> reported using BEt<sub>3</sub>, AlMe<sub>3</sub> and ZnEt<sub>2</sub> in solution phase as prospective reducing agents and obtained a copper deposit from ZnEt<sub>2</sub> but not from BEt<sub>3</sub> and AlMe<sub>3</sub>. A parasitic reaction was reported with ZnEt<sub>2</sub>, which leads to Zn impurity. A mechanistic study using Density Functional Theory (DFT) has been reported by Dey and Elliott<sup>9</sup> on these transmetallation reactions.

All the techniques mentioned above have high reaction temperatures. Knisley *et al.*<sup>10,11</sup> proposed a new technique for Cu ALD at low temperature. They have reported that the deposition starts from 80°C and that the growth rate becomes constant at

120°C, with no growth seen above 160°C. Each ALD cycle consists of three pulses: Cu(dmap)<sub>2</sub>, a protic acid (formic acid) and hydrazine. Knisley's proposal holds promise for deposition of other metals too. Initial deposition results were also reported from Ni<sup>(+2)</sup> complexes<sup>11</sup>.

The proposed overall reaction is as follows:



There is no direct evidence for the formation of copper formate at the surface in Knisley's work. However, Ravindranathan *et al.*<sup>12</sup> have shown by chemical analysis and infrared spectroscopy that an aqueous solution of copper formate undergoes rapid reduction to copper metal at ambient temperature upon treatment with hydrazine hydrate. Hydrazine has been used previously as a catalytic reducing agent for aromatic nitro compounds in the presence of finely divided metals<sup>13</sup>, but equation (1) implies that N is itself reduced along with Cu in this case. However, the mechanistic detail of this process is unknown and this forms the motivation for our work.

We apply Unrestricted DFT using the Perdew–Burke–Ernzerhof (PBE) functional<sup>14</sup> and the valence double- $\zeta$  with polarization def-SV(P) all-electron basis set<sup>15</sup>, as implemented in the TURBOMOLE program version 6.4<sup>16,17</sup>. A Cu<sub>55</sub> cluster coin with a (111) surface facet of C<sub>3v</sub> symmetry has been modelled so as to understand the adsorption of the compounds. All the adsorbed models were computed with zero total charge. The surface model has been used by Larsson *et al.*<sup>18</sup>. TURBOMOLE is limited to gas phase or cluster calculations. Therefore, in order to calculate total energies per Cu atom of bulk Cu metal for the reaction energies, we add the adhesion energy computed for bulk Cu<sub>(s)</sub> using the VASP code<sup>19</sup> with the same functional. The technique used here has also been reported in earlier studies<sup>9,20</sup>. In all the calculations no activation barrier for the reactions has been taken into account.

The entropy change for the reactions has also been calculated. This is done by vibrational analysis of the gas phase molecules using TURBOMOLE<sup>21</sup>. The entropy has been calculated at T=393 K as this is a typical target temperature for Cu ALD. It is assumed that S(Molecule+Coin)  $\approx$  S(Coin) + S<sub>vibr</sub>(Molecule) and so the entropy change is  $\Delta S_{\text{ad}} \approx -S_{\text{trans+rot}}(\text{Molecule})$ . This is because after the molecule is adsorbed onto the surface, it loses its translational and rotational degrees of freedom and this is probably the major contribution to the entropy change. *Ab initio* Molecular Dynamics

(aiMD) within the isothermal-isobaric ensemble as implemented in TURBOMOLE has been carried out for a set of model structures for duration of 2 ps.

## Results and Discussion

In order to understand the mechanism we will pose a series of questions in the following sections. Reactions that are thermodynamically favoured have negative reaction energies. The set of reactions presented here are the most energetically feasible ones out of the wide range that we have investigated.

### (i) How do precursor fragments interact with formic acid?

When Cu(dmap)<sub>2</sub> adsorbs to a Cu surface, its most stable state is found<sup>9,22</sup> to be Cu<sup>(+1)</sup>(dmap). Therefore, in order to understand the further interaction with formic acid, we have taken a model system that has one dmap ligand adsorbed to a Cu (111) surface. This shows an adsorption energy of  $\Delta E_{\text{ad}} = -647$  kJ/mol relative to the gas-phase dmap anion and cationic coin, **Error! Reference source not found.**(i).

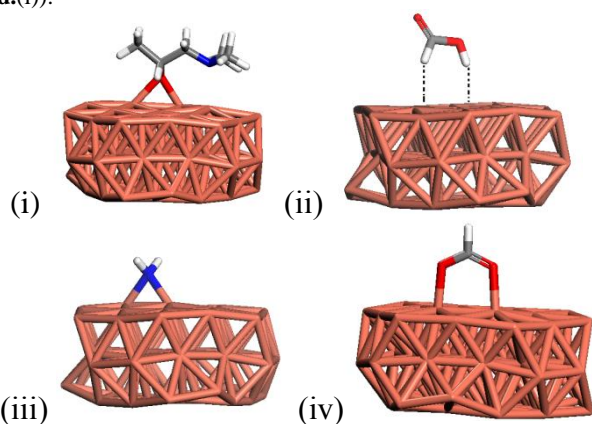


Figure 1: Optimized structure of (i) dmap ligand adsorbed on the smooth model copper surface, (ii) physisorbed formic acid (iii) adsorbed NH<sub>2</sub> radical, (iv) adsorbed formate anion. (**Error! Reference source not found.** for formate adsorption onto a rough surface). Colour code: brown=Cu, blue=N, red=O, grey=C, white=H.

To the optimised geometry of this adsorbate we brought in HCOOH (**Error! Reference source not found.**). During a 300 step MD study of 2 ps duration, at 393 K from this geometry, we see that the oxygen of the dmap anion on the surface spontaneously abstracts the protonic H from formic acid (floating near it) to form a protonated ligand dmap-H. The remaining formate anion (HCOO<sup>-</sup>) bonds with a copper atom on the surface. The adsorbed optimized structure of HCOOH shows a  $\Delta E_{\text{ad}} = -33$  kJ/mol onto the bare copper surface (**Error! Reference source not found.** (ii)). The adsorption energy of the formate anion alone is  $\Delta E_{\text{ad}} = -565$  kJ/mol relative to the gas-phase anion. The overall reactions with desorption of the dmap-H ligand and adsorption of formate anion may thus be written:  
 $\text{dmap}^{\text{(surf)}} + \text{HCOOH}_{(\text{g})} \rightarrow \text{dmap-H}_{(\text{g})} + \text{HCOO}^{\text{(surf)}} \dots (2)$   
 This reaction is computed to be exothermic:  $\Delta E = -56$  kJ/mol at  $T = 0$  K.

### (ii) In which form does the hydrazine react?

Hydrazine might disintegrate into active species when it comes in contact with the surface (surface catalysed reaction<sup>12</sup>) or else thermal energy might split the molecule in the gas phase already. In order to

find out what active species are likely to be present when hydrazine is admitted to the chamber, we have computed the possible dissociation reactions of hydrazine in the gas phase, as follows:  
 $\text{NH}_2\text{-NH}_2 \rightarrow 2\text{NH}_2$ ;  $\Delta E = +54.7$  kJ/mol (homolytic fission)...(3)  
 $\text{NH}_2\text{-NH}_2 \rightarrow \text{NH} + \text{NH}_3$ ;  $\Delta E = +44.9$  kJ/mol....(4)  
 $\text{NH}_2\text{-NH}_2 \rightarrow \text{N}_2 + 2\text{H}_2$ ;  $\Delta E = +209.8$  kJ/mol....(5)

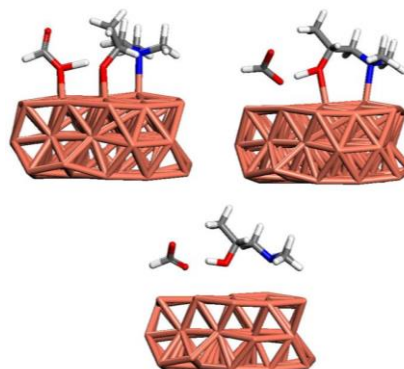


Figure 2: Some snapshots of MD simulation of dmap anion interacting with formic acid in order to form copper formate and dmap-H. The above structures are not optimized. Colour code: brown=Cu, blue=N, red=O, grey=C, white=H.

The  $T\Delta S$  ( $T = 393$  K) is 32.6 kJ/mol, 24.0 kJ/mol, 63.2 kJ/mol for equations 3, 4 and 5 respectively. Thus the entropy contribution makes the total  $\Delta G \sim 20$  kJ/mol for equations (3) and (4). However,  $\Delta G$  is  $> 140$  kJ/mol for equation (5). Hence this suggests that the formation of gas phase radicals NH<sub>2</sub> or NH is most favourable if there is some additional thermal energy. The use of NH<sub>2</sub> radicals in the formation of pure metals like Co has been investigated before by Hideharu *et al.*<sup>23</sup>

We compute the energy of adsorption of a NH<sub>2</sub> radical onto the Cu surface to be  $\Delta E_{\text{ad}} = -240$  kJ/mol (**Error! Reference source not found.** (iii)). Molecular adsorption of N<sub>2</sub>H<sub>4</sub> shows  $\Delta E_{\text{ad}} = -109$  kJ/mol. By Hess's law we see that surface formation of NH<sub>2(ads)</sub> from N<sub>2</sub>H<sub>4(ads)</sub> releases -316.3 kJ/mol of energy (**Error! Reference source not found.**). These high adsorption energies might indicate that N persists at the surface as an impurity in the film. However, we know that Cu<sub>3</sub>N is an unstable compound<sup>24</sup> and so ultimately N incorporation is probably not favoured. The formation of NH from N<sub>2</sub>H<sub>4</sub> is not explored as it is unreactive over a surface, which will be seen in the next section. Thus the disintegration of hydrazine takes place either in the gas phase into NH<sub>2</sub> and NH or over the surface into NH<sub>2</sub>.

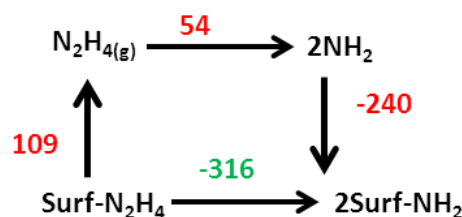
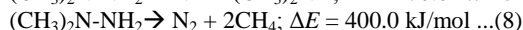
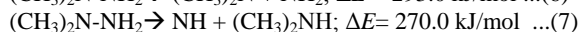


Figure 3: Hess cycle showing the formation of surface adsorbed NH<sub>2</sub> from surface adsorbed N<sub>2</sub>H<sub>4</sub>. All the energies are in kJ/mol of hydrazine.

The gas phase dissociation of 1,1-dimethyl hydrazine can be compared with that of NH<sub>2</sub>-NH<sub>2</sub>.



The  $T\Delta S$  for reaction (6) is 28.6 kJ/mol, for (7) is 20.4 kJ/mol and for (8) is 36.0 kJ/mol. Thus the entropy factor cannot overcome the reaction energies. This suggests that hydrazine is a better source of  $\text{NH}_x$  radicals ( $x=1, 2$ ) than substituted hydrazine.

### (iii) How do the $\text{NH}_x$ radicals react with copper formate?

To investigate the subsequent reactions, we have brought the NH and  $\text{NH}_2$  radicals close to the atoms of the adsorbed copper formate moiety from the previous reaction steps. The possible sites for NH and  $\text{NH}_2$  attack are Cu, O and H.

We see that when we bring the  $\text{NH}_2$  towards Cu, perpendicular to the plane of the adsorbed copper formate, it forms a Cu-N adduct, without any further change. When the radical is brought towards formate H or towards O in same plane as the formate moiety (**Error! Reference source not found.**), it abstracts the H and spontaneously forms  $\text{NH}_3$  and  $\text{CO}_2$  during the geometry optimization.

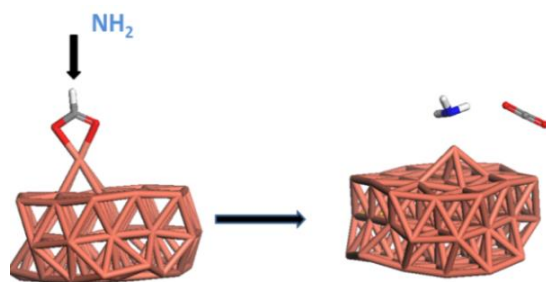


Figure 4: When the  $\text{NH}_2$  radical attacks the H of  $\text{Cu}(\text{HCOO})$ , it forms  $\text{CO}_2$  and  $\text{NH}_3$  as by-products, leaving an atom of copper metal on the surface. Colour code: brown=Cu, blue=N, red=O, grey=C, white=H.

For this surface reaction we compute the following energy change  $\text{Cu}^{(+1)}\text{OOCH}_{(\text{surf})} + \text{NH}_2(\text{g}) \rightarrow \text{Cu}^{(0)}(\text{s}) + \text{CO}_2(\text{g}) + \text{NH}_3(\text{g})$   
 $\Delta E = -467 \text{ kJ/mol} \dots (9)$

The  $T\Delta S$  for this reaction is 78.7 kJ/mol at  $T = 393 \text{ K}$ . Thus  $\Delta G$  is -545.7 kJ/mol for the overall reaction. Here we see that the C in  $\text{Cu}^{(+1)}\text{OOCH}$  is in its +2 oxidation state and transforms to +4 oxidation state in  $\text{CO}_2$  giving away one electron to  $\text{N}^{(-2)}\text{H}_2$  to form  $\text{N}^{(-3)}\text{H}_3$  and another electron to  $\text{Cu}^{(+1)}$  to form  $\text{Cu}^{(0)}$ .

In a similar way, the NH radical was placed in a plane perpendicular to the copper formate at different positions, close to Cu, H and O. In all the cases we find that the NH moves close to the surface atoms and away from the adsorbed copper formate. The NH then attaches itself to the coordinatively unsaturated Cu atoms on the surface.

Finally, we compute the adsorption energy of the by-products:  $\Delta E_{\text{ad}}(\text{NH}_3) = -42.0 \text{ kJ/mol}$  and  $\Delta E_{\text{ad}}(\text{CO}_2) = +23.0 \text{ kJ/mol}$  at  $T=0 \text{ K}$ . At  $T=393 \text{ K}$  the  $T\Delta S$  is 95.8 kJ/mol for  $\text{NH}_3$ <sup>20</sup> and for  $\text{CO}_2$  is 39.7 kJ/mol. Hence the adsorption of these by-products is thermodynamically not favoured.

Redistribution of the reaction energy from equation (9) would thus be sufficient to break even the N-N bond in hydrazine (~50 kJ/mol, equation 3) and desorb the by-products from the surface.

We have observed in the above reactions that surface intermediates like  $\text{NH}_2$  radicals are formed after the dissociation of the hydrazine molecule. This radical reacts spontaneously with the formate to deposit copper and produce  $\text{CO}_2$  and  $\text{NH}_3$  by-products. This provides evidence that equation (1) takes place as proposed by

Knisley *et al.* We calculate that  $\Delta E = -172 \text{ kJ/mol-Cu}$  at  $T=0 \text{ K}$  for equation (1) by making use of the adhesion energy of bulk Cu of -320 kJ/mol-Cu calculated with VASP<sup>9</sup>.

### (iv) How does hydrazine react with higher acid copper compounds?

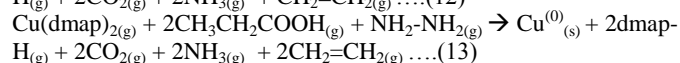
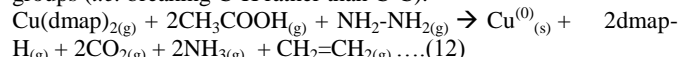
It is interesting to ask whether other protonic acids can function in the same way as formic acid in this process. The above reaction (1) was altered so as to consider acetic acid following the equation  $\text{Cu}(\text{dmap})_2(\text{g}) + 2\text{CH}_3\text{COOH}(\text{g}) + \text{NH}_2\text{-NH}_2(\text{g}) \rightarrow \text{Cu}^{(0)}(\text{s}) + 2\text{dmap-H}(\text{g}) + 2\text{CO}_2(\text{g}) + 2\text{CH}_3\text{-NH}_2(\text{g}) \dots(10)$

and for propanoic acid according to  $\text{Cu}(\text{dmap})_2(\text{g}) + 2\text{CH}_3\text{CH}_2\text{COOH}(\text{g}) + \text{NH}_2\text{-NH}_2(\text{g}) \rightarrow \text{Cu}^{(0)}(\text{s}) + 2\text{dmap-H}(\text{g}) + 2\text{CO}_2(\text{g}) + 2\text{CH}_3\text{CH}_2\text{-NH}_2(\text{g}) \dots(11)$ .

This assumes that the  $\text{NH}_2$  radical abstracts an alkyl radical from adsorbed acetate or propanoate, breaking a C-C bond. The computations yielded  $\Delta E = -58 \text{ kJ/mol}$  for equation (10) and  $-98 \text{ kJ/mol}$  for equation (11). These ALD reaction energies are less negative than that of equation (1), which may be attributed to the cost of breaking the strong C-C bond in these acids.

To investigate this reaction pathway, we bring the  $\text{NH}_2$  radical near to the structure of adsorbed copper acetate, and observe during geometry optimization that the  $\text{NH}_2$  radical coordinates with the coordinatively unsaturated surface copper atoms, rather than spontaneously abstracting the methyl radical. Thus, although the overall ALD reaction energy is moderately exothermic, energy barriers exist that make the surface-mediated reaction with higher acids less likely to take place than the previous case of  $\text{HCOOH}$ . Nevertheless, the overall exothermicity indicates that the reaction might proceed via this mechanism in the solution phase, as mentioned by Knisley *et al.*<sup>11</sup>.

Another pathway for the higher acids is shown in equation (12) and (13) that proposes reductive elimination of H from the alkyl groups (*i.e.* breaking C-H rather than C-C).



We compute  $\Delta E = +18 \text{ kJ/mol}$  for reaction (12) and  $+90 \text{ kJ/mol}$  for (13) indicating that these reactions are endothermic and less probable than reactions (10) and (11).

### Conclusion

DFT calculations have been used to investigate the surface reactions of a three step ALD process for the deposition of Cu as proposed by Knisley *et al.*. Those authors proposed the formation of intermediate Cu formate at the surface and its reaction with hydrazine. Here, we confirm the stability of the formate intermediate and find the atom-by-atom mechanism for the reaction with hydrazine and deposition of Cu metal. All the elemental reaction steps are computed to be exothermic.

In a parallel study, it has been computed that the  $\text{Cu}(\text{dmap})_2$  precursor adsorbs strongly to the surface, which is the first step of the ALD cycle. In the second step formic acid is pulsed into the chamber. It has been observed in our simulation that the dmap ligand abstracts the protonic H from formic acid and desorbs as dmap-H, leaving formate adsorbed to the surface. In the final step, hydrazine is pulsed into the chamber and probably dissociates at the surface to form the  $\text{NH}_2$  radical. This radical abstracts  $\text{H}^{(0)}$  from the formate anion. Spontaneous decomposition of the resulting anion to  $\text{CO}_2$  causes reduction of a surface metal cation to  $\text{Cu}^{(0)}$ . The predicted by-products are  $\text{NH}_3$  and  $\text{CO}_2$ . Hydrazine partially oxidises formate,

which through its complete decomposition to CO<sub>2</sub> reduces Cu<sup>(+1)</sup> to Cu<sup>(0)</sup> (Figure 5). This suggests that the search for co-reagents in metal ALD should not be limited to traditional reducing agents like H<sub>2</sub>, but can also include reagent combinations that release electrons during oxidative decomposition.

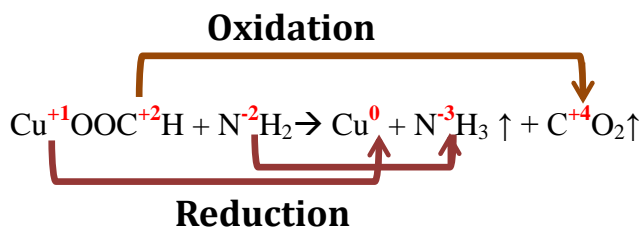


Figure 5: Redox reaction of equation 1

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(1) International Technology Roadmap for Semiconductors <http://www.itrs.net/>, 2011.

(2) Pathangey, B.; Solanki, R. *Electrochemical and solid state letters* **2000**, 3, 479.

(3) Mårtensson, P.; Larsson, K.; Carlsson, J.-O. *Applied Surface Science* **1998**, 136, 137.

(4) Hsu, I. J.; McCandless, B. E.; Weiland, C.; Willis, B. G. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2009**, 27, 660.

(5) Lee, B. H.; Hwang, J. K.; Nam, J. W.; Lee, S. U.; Kim, J. T.; Koo, S.-M.; Baunemann, A.; Fischer, R. A.; Sung, M. M. *Angewandte Chemie International Edition* **2009**, 48, 4536.

(6) Thompson, J. S.; Zhang, L.; Wyre, J. P.; Brill, D. J.; Lloyd, K. G. *Thin Solid Films* **2009**, 517, 2845.

(7) Vidjayacoumar, B.; Emslie, D. J. H.; Clendenning, S. B.; Blackwell, J. M.; Britten, J. F.; Rheingold, A. *Chemistry of Materials* **2010**, 22, 4844.

(8) Vidjayacoumar, B.; Emslie, D. J. H.; Blackwell, J. M.; Clendenning, S. B.; Britten, J. F. *Chemistry of Materials* **2010**, 22, 4854.

(9) Dey, G.; Elliott, S. D. *The Journal of Physical Chemistry A* **2012**, 116, 8893.

(10) Knisley, T. J.; Kalutarage, L. C.; Winter, C. H. *Coordination Chemistry Reviews* **2013**, 257, 3222.

(11) Knisley, T. J.; Ariyasena, T. C.; Sajavaara, T.; Saly, M. J.; Winter, C. H. *Chemistry of Materials* **2011**, 23, 4417.

(12) Ravindranathan, P.; Patil, K. C. *Thermochimica Acta* **1983**, 71, 53.

(13) Furst, A.; Berlo, R. C.; Hooton, S. *Chemical Reviews* **1965**, 65, 51.

(14) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996**, 77, 3865.

(15) Schafer, A.; Horn, H.; Ahlrichs, R. *The Journal of Chemical Physics* **1992**, 97, 2571.

(16) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chemical Physics Letters* **1989**, 162, 165.

(17) Schafer, A.; Huber, C.; Ahlrichs, R. *The Journal of Chemical Physics* **1994**, 100, 5829.

(18) Larsson, J. A.; Elliott, S. D.; Greer, J. C.; Repp, J.; Meyer, G.; Allenspach, R. *Physical Review B* **2008**, 77, 115434.

(19) Kresse, G.; Hafner, J. *Physical Review B* **1994**, 49, 14251.

(20) Dey, G.; Elliott, S. *Theor Chem Acc* **2013**, 133, 1.

(21) Deglmann, P.; May, K.; Furche, F.; Ahlrichs, R. *Chemical Physics Letters* **2004**, 384, 103.

(22) Coyle, J. P.; Dey, G.; Sirianni, E. R.; Kemell, M. L.; Yap, G. P. A.; Ritala, M.; Leskelä, M.; Elliott, S. D.; Barry, S. T. *Chemistry of Materials* **2013**, 25, 1132.

(23) Shimizu, H.; Sakoda, K.; Momose, T.; Koshi, M.; Shimogaki, Y. *J. Vac. Sci. Technol. A* **2012**, 30.

(24) Gonzalez-Arrabal, R.; Gordillo, N.; Martin-Gonzalez, M. S.; Ruiz-Bustos, R.; Agullo-Lopez, F. *Journal of Applied Physics* **2010**, 107, 103513.