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# Steric and electronic interactions between source gas and substrate surface during the Al-CVD/Al selective epitaxy process as investigated by quantum chemical calculations

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## Abstract

We have performed quantum chemical calculations by semiempirical MNDO and by density functional theory (DFT) to rationalize the selection of an Al source gas for the selective Al-CVD/Al process. The electronic properties of $Al(CH_3)_nH_{3-n}$, ($n = 0$ to 3) and their adsorption complexes over representative aluminum metal clusters were calculated. Initially, the interaction of Al source gases with a representative Al metal was studied by both MNDO and DFT methods and the results were found to be qualitatively comparable. Further detailed calculations were performed by MNDO to understand the interaction of $Al(CH_3)_nH_{3-n}$ with larger cluster models of Al substrate as well as insulator silica surface. The results of the calculations indicate that the interaction energy between the substrate and the source are controlled by both steric and electronic factors. The steric factor favors the interaction of unsubstituted hydride, namely aluminum trihydride and the electronic factor favors the interaction of maximum substituted aluminum organic, namely trimethyl aluminum with the substrates. However, dimethyl aluminum hydride has the most favorable interaction energy with the Al metal, since it has the right combination of steric and electronic factors. The interaction energy of DMAH with chlorided silica surface is more favorable than the untreated silica surface.

## 1. Introduction

Attempts to fabricate very large scale integrated (VLSI) circuits are made with different technologies using a variety of materials [1]. In recent times, the chemical vapor deposition (CVD) technique for filling of via holes, i.e. holes filled with conductors and connected to both lower and upper wirings, has been investigated [2]. Tungsten plugging into the holes is the major method utilized in production lines, so far. It is called the blanket W-CVD/etch-back process and it is usually performed by depositing W on wafers and then removing W from the areas except from the holes by etching-back. However, this technology has shortcomings of the process complexity, which raises the fabrication cost and Al/W or W/TiN/Al interfaces which lead to an increase in resistance and degradation of electromigration [3].

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Selective Al-CVD has been developed as a promising alternative technique to the current via-filling technology, because of its advantages over conventional W-CVD processes [4,5]. Al plugging has two major applications, namely the deposition on Si [6,7] for contacts and for the deposition on Al for vias [5,8]. Many source gases such as alkyl chlorides, trialkyl aluminums, hydrides and amine adducts were examined for the selective Al deposition [5–12]. In this paper, we report the results of quantum chemical (QC) calculations performed to understand which of the chemical species is preferable among the homologous series $Al(CH_3)_nH_{3-n}$ ($n = 0$–$3$) for selective epitaxy deposition of aluminum.

## 2. Method

The semiempirical quantum chemical MNDO (modified neglect of differential overlap) calculations were carried out by the standard procedure of Dewar and Thiel [13] and the AMPAC code (QCPE Program 506) was used. DFT (density functional theory) quantum chemical calculations [14] were performed using the DMOL package. The calculations were carried out using a double numeric basis set [15] including polarization functions and a JMW-type local correlation functional were used for exchange correlation energy terms in the total energy expression. The above calculations were carried out using the commercial software package of Biosym Technologies, Inc., USA in a Silicon Graphics IRIS workstation.

A series of calculations on numerous cluster models were planned to investigate the interaction of methyl aluminum hydrides with substrate surfaces. Due to computational efficiency, we adopted to the well established MNDO calculations. However, we carried out accurate DFT calculations for the aluminum methyls and the model clusters representing their adsorption over an aluminum metal. The results of the geometry optimization calculations for the aluminum methyls using both the MNDO and DFT methods were similar. It was observed that the equilibrium bond angles predicted by both the methods are very close and the bond lengths predicted by the DFT method were always longer, typically by 0.1 Å. The electronic properties were qualitatively the same as discussed in the next section. Since these results suggest that a reliable correlation could be obtained by the MNDO method, we adopted MNDO for further investigations.

## 3. Results and discussion

### 3.1. The electronic properties of aluminum methyls

The values of total energy and the net charge density on various atoms derived by Mulliken population analysis for the homologues, $Al(CH_3)_nH_{3-n}$ ($n = 0$–$3$) are shown in Table 1. The results of the calculations by both MNDO and DFT methods are included for comparison and the qualitative trends predicted by both methods are in satisfactory agreement. The $Al_{substrate}$–$Al_{source}$, Al–C and Al–H distances predicted by MNDO are typically 2.51, 1.83 and 1.50 Å. Aluminum trihydride (ATH) has a planar structure, while methyl substitution for hydrogen atoms causes a slight deviation from planarity and the central aluminum has $sp^2$ hybridization. The net charge on the central aluminum is positive, while the hydrogen or methyl groups have a negative charge. The hydrogens are more effective in withdrawing electrons from the aluminium than the methyl group, thus Al in ATH has the highest positive charge,

Table 1
The electronic properties of the aluminum methyls

| $Al(CH_3)_nH_{3-n}$ | | Total energy | | $q_{Al}$ | | $q_H$ | | $q_{CH_3}$ | |
|---|---|---|---|---|---|---|---|---|---|
| $n$ | compound | MNDO (eV) | DFT (au) | MNDO | DFT | MNDO | DFT | MNDO | DFT |
| 0 | ATH | −89.38 | −243.11 | +0.83 | +0.40 | −0.28 | −0.13 | – | – |
| 1 | MMAH | −246.56 | −282.10 | +0.76 | +0.38 | −0.27 | −0.11 | −0.23 | −0.17 |
| 2 | DMAH | −403.74 | −321.08 | +0.69 | +0.33 | −0.26 | −0.10 | −0.22 | −0.17 |
| 3 | TMA | −560.89 | −360.07 | +0.62 | +0.30 | – | – | −0.21 | −0.16 |

while Al in trimethyl aluminum (TMA) has the lowest positive charge as shown in Table 1.

### *3.2. The interaction of the aluminum methyls with a single Al atom*

The electronic properties of the adsorption complex between aluminum metal and aluminum methyls, calculated by both MNDO and DFT calculations are shown in Table 2. The net charges on the Al substrate are positive as the electron transfer occurs from the substrate to the source material. Such electron transfer is expected to be more facile in the case of ATH than TMA, based on the net charges reported in Table 1. The net charges predicted by both the methods for the source Al are different and this is an indication of the poor performance of the MNDO method to predict the polarization. We calculated the interaction energy of the aluminum methyls with an Al according to the relation:

$$\text{Interaction energy} = \left(E_{\text{Al + aluminum methyl}}\right) - \left(E_{\text{aluminum methyl}} + E_{\text{Al}}\right),$$

where $E$ is the total energy. The variation of the interaction energy of aluminum methyl with Al, as a function of the number of methyl groups is shown in Fig. 1. Although a linear relation is expected based on the Coulombic forces between the calculated net charges, the observation showed a minimum with respect to the number of methyl groups. Dimethyl aluminum hydride (DMAH) is found to have the most favorable interaction energy. The results in Fig. 1 indicate that the interaction energy is controlled by more than one factor and the Coulombic force is just one among them. The interaction energy calculated by MNDO and DFT methods are in close agreement. The ease of transfer of electrons from the substrate to the source which facilitates the dissociation of the aluminum methyls, is also dependent on the energy of the highest occupied molecular orbital (HOMO) of the Al substrate and the lowest unoccupied molecular orbital (LUMO) of the aluminum methyls. The LUMO of aluminum methyls is stabilized by the methyl substitution and thus the electron transfer is most favorable for the trimethyl aluminum. Thus the Coulombic attraction and the ease of transfer of electrons are acting in opposite directions as the methyl substitution increases.

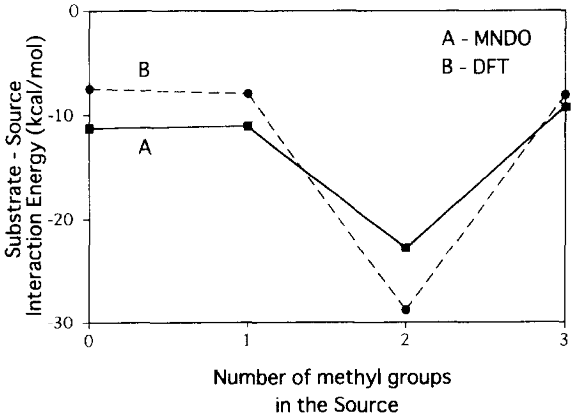


Fig. 1. The variation of the interaction energy between aluminum methyl and an aluminum atom as a function of the number of methyls groups in the source, namely $Al(CH_3)_nH_{3-n}$. The various aluminum methyl sources are when $n = 0$, aluminum trihydride (ATH); $n = 1$, monomethyl aluminum hydride (MMAH); $n = 2$, dimethyl aluminum hydride (DMAH) and $n = 3$, trimethyl aluminum hydride (TMA). The interaction energy calculated by both MNDO (A) and DFT (B) methods are shown.

### *3.3. The interaction of the aluminum methyls with an $Al_n$ cluster*

The interactions of aluminum methyls with an Al metal surface containing many atoms, namely $Al_n$,

Table 2

The electronic properties of Al + aluminum methyls

| $Al(CH_3)_nH_{3-n}$ | | Total energy of Al + aluminum methyls | | $q_{\text{Al substrate}}$ | | $q_{\text{Al source}}$ | |
|---|---|---|---|---|---|---|---|
| $n$ | compound | MNDO (eV) | DFT (au) | MNDO | DFT | MNDO | DFT |
| 0 | ATH | −134.35 | −484.47 | +0.53 | +0.23 | +0.01 | +0.07 |
| 1 | MMAH | −291.52 | −523.43 | +0.55 | +0.21 | −0.01 | +0.08 |
| 2 | DMAH | −449.21 | −562.41 | +0.58 | +0.22 | −0.10 | +0.16 |
| 3 | TMA | −605.77 | −601.37 | +0.59 | +0.24 | −0.15 | +0.20 |

where $n = 5$, 10 and 14, were also studied. These calculations were carried out with the aim of studying the effect of steric interactions of the substituted methyl groups. The influence of the substitution on the interaction energy was studied by considering the adsorption of aluminum methyls on an $Al_5$ surface as shown in Fig. 2. The atom positions of the substrate are according to the aluminum crystal structure. Geometry optimization calculations were attempted and it was observed that the methyl groups tend to deviate away from the substrate aluminum. More deformation of the source gas was observed indicating the easier dissociation of the substrate as it approaches the substrate. However, since our interests are to estimate the substrate–source interaction energy, the $Al_{substrate}$–$Al_{source}$ distance was assigned the optimized distances obtained for the systems given in Table 2. The calculated total and interaction energy values for complexes shown in Fig. 2 are given in Table 3. The interaction energy is again favorable for DMAH among the methyl substituted cases, while ATH has the most favourable interaction energy. Thus the steric interactions are significant in addition to the electronic interactions. However, it must be noted that ATH poses problems on practical applications, since it is not stable at ambient conditions. They have to exist as an adduct of other

Table 3
The energetics of $Al_5$ cluster + aluminum methyls

| $Al(CH_3)_nH_{3-n}$ | | Total energy of $Al_5$ + aluminum methyls (eV) | Interaction energy (kcal/mol) |
|---|---|---|---|
| $n$ | compound | | |
| 0 | ATH | −316.90 | −12.68 |
| 1 | MMAH | −473.72 | −4.15 |
| 2 | DMAH | −630.98 | −6.23 |
| 3 | TMA | −786.46 | +9.22 |

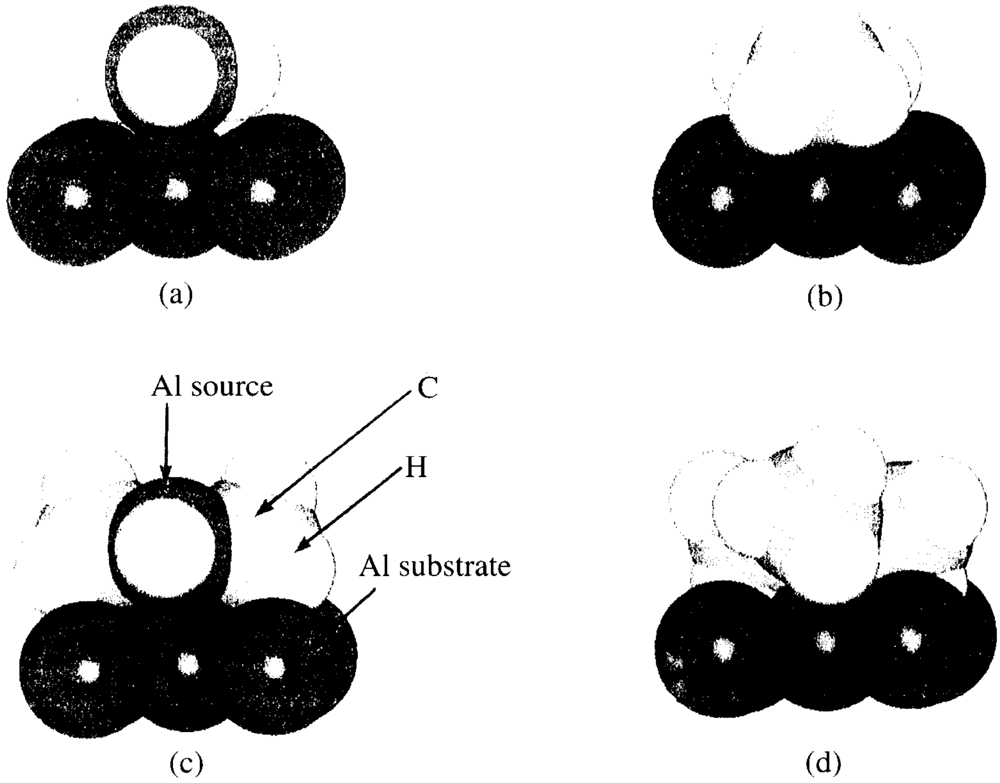


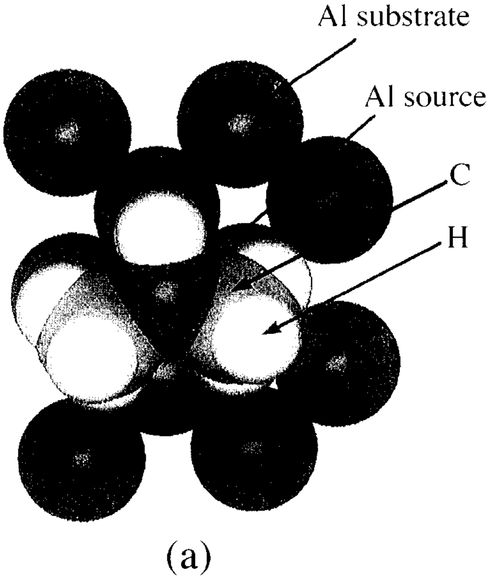
Fig. 2. Various aluminum methyl sources ATH (a), MMAH (b), DMAH (c) and TMA (d) adsorbed over an $Al_5$ cluster. The nomenclature of source gases are the same as Fig. 1.

organic compounds which lead to impurity phases during the chemical vapor deposition (CVD) process. The large unfavorable interaction energy observed for the $Al_5$–TMA system also emphasizes the importance of steric interactions.

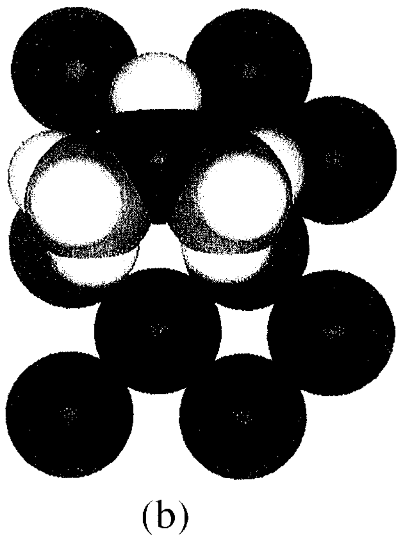
The interaction of DMAH with an Al metal surface is analyzed in more detail by extending the number of surface atoms and bulk atoms by considering $Al_{10}$ and $Al_{14}$ cluster models to represent the metal. In the $Al_{10}$ system, we have studied two possible interaction models of DMAH molecules as shown in Figs. 3a and 3b. In Fig. 3a, the Al of DMAH is interacting with the metal surface through a four-fold bridge site which will lead to epitaxial growth. In Fig. 3b the Al of DMAH is directly interacting with an Al atom of the metal surface. This is an 'on-top' site interaction which will lead to non-epitaxial growth of aluminum. In this configuration the methyl groups are in eclipsed configuration with other Al metals on the surface. The interaction energy calculated for both these systems were endothermic (Table 4), however the epitaxy mode was relatively more favorable than the non-epitaxy mode by 7.14 kcal/mol. Furthermore, in the configuration shown in Fig. 3b, the DMAH was rotated along the $Al_{substrate}$–$Al_{source}$ axis. This led to a configuration in which the methyl groups are in a staggered configuration and the steric repulsion was found to be less in this configuration as predicted by a favorable interaction energy. An $Al_{14}$ cluster, consisting two more layers of 4 atoms and 5 atoms, respectively in addition to the $Al_5$ cluster (Fig. 2) was also considered. The energy values calculated for the interaction of DMAH with aluminum clusters of various sizes are listed in Table 4. It can be observed that increasing the number of substrate atoms laterally on the surface ($Al_{10}$) makes the interaction energy less favorable, while increasing the number of substrate atoms in the bulk layers ($Al_{14}$) leads to favorable interaction energy relative to the $Al_{10}$ cluster. Thus the steric repulsions between the methyl group and the surface atoms acting in an unfavorable way is reconfirmed by these results.

Table 4
The energetics of $Al_n$ cluster + DMAH

| $Al_n$ cluster | Total energy of $Al_n$ + DMAH (eV) | Interaction energy (kcal/mol) |
|---|---|---|
| $Al_1$ | −449.21 | −22.83 |
| $Al_5$ | −630.98 | −6.23 |
| $Al_{10}$ (epitaxy) | −855.00 | +37.59 |
| $Al_{10}$ (non-epitaxy) | −854.69 | −44.74 |
| $Al_{14}$ | −1045.74 | +21.68 |



(a)



(b)

Fig. 3. The epitaxy (a) and non-epitaxy (b) modes of DMAH adsorbed over an $Al_{10}$ cluster.

### *3.4. The interaction of the aluminum methyls with a silica cluster*

In the process to form direct contact CVD-Al/Al, deposition is expected only on metal surfaces and not over the insulating layer, $SiO_2$. However, growth of Al on $SiO_2$ has been observed, when the surfaces are treated for a longer time by reactive ion etching using chlorinating gases such as $BCl_3$ [16]. In order to understand the influence of chlorine, we calculated the interaction of DMAH with an amorphous silica surface represented by the siloxane-type ($H_6Si_2O_7$) and a chlorinated silica surface represented by chlorosiloxane-type ($ClH_5Si_2O_7$) clusters as shown in Figs. 4a and 4b, respectively. The positive charge on the silicon atom was decreased by the presence of a chlorine atom in the chlorosiloxane. It is widely known that treatment with halide ions leads to oxygen deficiency. After halide treatment, the existence of a $Cl^-$ ion in silica and defects leading to the formation of a Si–Si link have been reported to cause a dielectric breakdown [17]. The interaction of DMAH with the $SiO_2$ surface (Fig. 4a) was highly exothermic (interaction energy = 24.03 kcal/mol), while with that of the chlorinated surface (Fig. 4b) was still exothermic (interaction energy = 11.78 kcal/mol), but energetically more favourable than in the previous case. However, at this stage it is not possible to compare these values with the interaction energy with aluminum metal, since the calculated interaction energy values are depending on the cluster size and the configuration. Although calculations on larger cluster models and optimization of the configuration of adsorption complexes are needed for a complete understanding, the present calculations provide a qualitative reasoning for the deposition of Al over chlorinated silica, rather than over untreated silica. Thus Al deposition can occur over the chlorinated silica, thereby decreasing the selectivity of the CVD-Al/Al process.

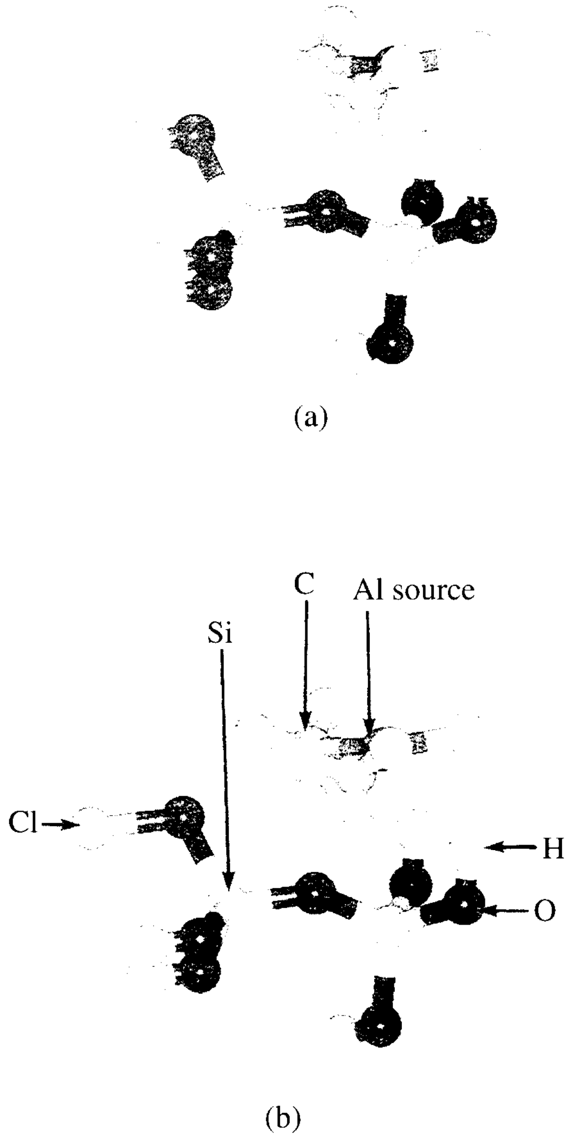


Fig. 4. The DMAH adsorbed over cluster models representing untreated silica (a) and chlorinated silica (b) surfaces.

## 4. Conclusions

The above studies on the interaction of aluminum methyl source gas with aluminum substrate and silica substrate using quantum chemical calculations have led to the following conclusions: (1) *DMAH is the suitable choice for selective Al-CVD on Al substrate*, among the homologous series $Al(CH_3)_nH_{3-n}$, where $n = 0$ to 3, (2) the interaction energy between the substrate and the source is controlled by both steric and electronic factors and (3) the interaction energy of DMAH with chlorinated silica is relatively favorable compared to an untreated silica surface.

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