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AB INITIO STUDIES OF SILVER PRECURSOR FOR FEBID: $Ag(PMe_3)_n$ n=2,3,4

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Abstract. The detailed structure, thermal and chemical stability of the $Ag(PMe_3)_n$ compounds were studied by applying quantum chemical method. The results obtained showed that $Ag(PMe_3)_2$ and $Ag(PMe_3)_4$ could be used as precursors for FEBID. The appearance energy of Ag was evaluated to find the most promising dissociation ways.

Keywords: Ag compound, DFT calculation, dissociation, precursor

1. Introduction

Currently, the investigation of magnetic nanostructures is one of the most active topics in condensed-matter and materials-science research, offering many opportunities [1]. The magnetic nanostructures could be applied, for example, in high-density information storage and magnetic sensing, magnetic logic, radio-frequency oscillators, giant or tunnel magnetoresistance and Hall sensors, etc. [2]. Many of the devices in the field of magnetic nanostructures are designed by various techniques such as: thin-film growth, micro nano-, optic-litography, sputtering, thermal or electron beam evaporation, molecular beam epitaxy, pulsed laser deposition, etc. [3,4]. However, the usage of these techniques has disadvantages such as resolution, roughness, shape, materials involved, modification of magnetic properties, cost, etc. [2]. In this content new techniques are becoming promising route for the direct growth of magnetic nanostructures in a single step. One of these techniques is focused electron beam induced deposition (FEBID). This technique allows one to deposit the structures on the nanometer scale. FEBID is an emerging chemical vapor deposition method, which enables resist-free ‘direct-write’ additive nanomanufacturing using a variety of materials with a high degree of spatial and time-domain control. The possibility to deposit very small amounts of material for tuning purposes on a fully processed micro/nanodevice at the right place, with control, and without damage to surrounding sensitive areas can be very cost effective even if the speed of the deposition is very low compared to standard photolithography [5]. However, this new technology relies on precursors that are not optimized for the electron driven process. The number of these precursors is limited to a few, although the number of references in this field of research has strongly increased during last years. One of the most important choices of the precursors for FEBID is the chemical composition of the actual precursor molecule, i.e. the element(s) for the deposition. Other secondary parameters that determine the choice of the precursor molecule are as follows: vapor pressure as a function of temperature, chemical stability, sticking coefficient / residence time of the precursor molecules on the sample, system behavior and practical aspects such as: toxicity issues and ability to pump out precursor molecules after use and possible contamination of the system [6].

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Hence, the aim of our study is to determine the properties of $Ag(PMe_3)_2$, $Ag(PMe_3)_3$ and $Ag(PMe_3)_4$ aiming to suggest a new Ag precursor for FEBID. We investigate thermal and chemical stability, toxicity and the energy of the appearance fragments of the $Ag(PMe_3)_2$, $Ag(PMe_3)_3$ and $Ag(PMe_3)_4$. The results of the computer simulation of Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3) are used to compare the properties of the derivatives under investigation. We choose Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3) because it is showed that this derivative could be a precursor of Ag [7].

2. Method of investigation

The structure of the molecule and its fragments has been studied by the Becke's three-parameter hybrid functional applying the non-local correlation provided by Lee, Yang, and Parr (B3LYP) [8], – a representative standard DFT method. The most significant advantage of the DFT method is a significant increase in computational accuracy without the additional increase in computing time. Our investigation was performed with the 3-21G for Ag and 6-31++G**. The structure parameters of the molecule and its fragments under study have been optimized with no symmetry constraint. The vibration frequencies were investigated to check the accuracy of optimization results. The zero-point energy was included in the evaluation of the energy of appearance. This energy was calculated as the difference between the total energy of the molecule and the sum of the total energies of the fragments predicted. The calculations for the final states of the compounds are presented for the case of dissociation without taking into account the activation energy of the reverse reaction (E_r). In order to model the all-possible fragmentation processes for the pure Ag formation, we investigated the neutral dissociation, disociative ionization and bipolar dissociation (ion pair formation) taking into account that:

i. Ag positive/negative ions or neutral atom are formed from the molecule directly, i.e. the $Ag(PMe_3)_n$ (n=2,3,4)derivative loss Ag under electron impact;

ii. $Ag(PMe_3)_n$ (n=1,2,3) positive/negative or neutral fragment is formed, while Ag positive/negative ion or neutral atom occurs during the second step of fragmentation, i.e. the cascade- fragmentation is investigated. It is necessary to mention that the ionization potential of the derivatives was also obtained. This parameter was necessary to select the processes of the cation formation, i.e. the cations cannot form when the energy of their appearance is below the first ionization potential.

The electronegativity, chemical hardness and chemical softness were calculated as follows:

$\chi=-\frac{I+A}{2}$ (electronegativity);

$\eta=\frac{I-A}{2}$ (chemical hardness);

$S=\frac{1}{2\eta}$ (chemical softness),

where I and A are the ionization potential and the electron affinity. The ionization potential and affinity were calculated as the energy difference of ionized and neutral molecules.

Using this methodology, we took into account the processes when the molecular ions, formed with energy in excess of the ionization potential, may have no sufficient energy to be decomposed according to the lowest energy pathway. The Gaussian program packages were applied here [9].

3. Results and discussions

The obtained structures of the compound investigated are presented in Fig. 1. It can be seen that Ag and PMe_3 could form slightly-disordered linear, trigonal planar and tetrahedral coordination compounds. An analysis of the oxidation states indicates that the oxidation number of Ag in these compounds is different. It is −1 in $Ag(PMe_3)_2$, and +1 in the rest compounds under investigation. We emphasize that the +1 oxidation state of silver is predominant although its other oxidation numbers, such as −2, –1, 1, 2, 3 are also known [10]. Hence, this unusual form of the linear compound obtained could be related with uncommon oxidation state of Ag.

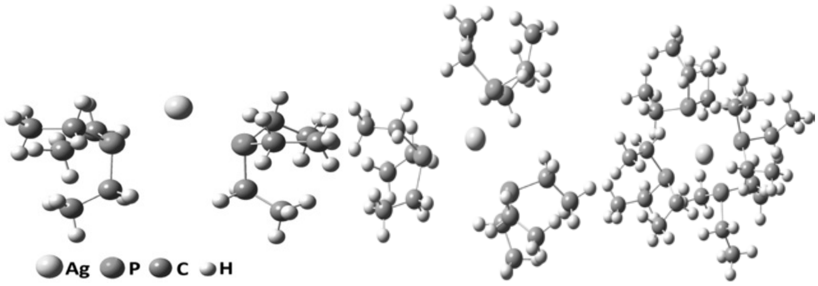

Fig. 1. View of $Ag(PMe_3)_2$ (on the left), Ag(PMe3)3 (in the center) and $Ag(PMe_3)_4$ (on the right)

As it was mentioned, the relatively high thermal stability is one of the requirements for the precursor [6]. It implies that derivatives are stable (preferable at room temperature) when stored in a reservoir. Hence, we calculated the binding energy per atom to compare the thermal stability of the derivatives investigated (Table 1). The binding energy per atom of Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3), which is stable in air, is smaller than that of $Ag(PMe_3)_2$ and $Ag(PMe_3)_4$ derivatives investigated. It leads to a conclusion that the thermal stability of them is high and it is possible to predict that these compounds could be stable in air, too. However, the thermal stability of $Ag(PMe_3)_3$ is lower that of the other compound under investigation. Therefore, its usage as a precursor of Ag is limited.

Table 1. Binding energy per atom, hardness, softness and electronegativity of the derivatives investigated

Derivatives	Binding energy per atom, eV	HOMO-LUMO gap, eV	Hardness, eV	Softness, eV	Maximum hardness index Y	Electronegativity, eV
$Ag(PMe_3)_2$	6.88	1.79	1.55	0.32	0.79	1.08
$Ag(PMe_3)_3$	4.43	1.17	0.59	0.85	-0.45	1.17
$Ag(PMe_3)_4$	7.53	0.65	1.02	0.33	0.78	1.53
Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3)	6.27	4.88	3.65	0.13	0.97	3.73

Referring to I. Utke et al. studies, pure materials can be obtained in the case when a chemical reaction is initiated by electrons [5], i.e. a precursor should be also chemically stable. The values of hardness and softness, presented in Table 1, indicate high chemical stability of Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3) what coincides with the results presented in Ref. [11] and indicates reliability of the approach applied. However, the chemical stability of $Ag(PMe_3)_n$ (n=2,3,4) is lower than that of Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3). This indicates the comparison of the values of chemical hardness, softness and HOMO-LUMO gap. These data are not enough for making conclusions on the chemical stability of $Ag(PMe_3)_n$ (n=2,3,4) because there is no evidence that these compounds are chemically unstable. Hence, the maximum hardness index Y was calculated too, as follows:

$Y=1-2S^{2\cdot}$

It is exhibited that hard-hard binding frame is preferred for the molecules which index Y holds values over 0.5 [12]. The chemical bond can still be formed as the soft-soft combination in the molecules where Y stands below 0.5 values, however, with positive nonzero figures. Only negative values of Y indicate anti-bonding character that can further be associated with anti-binding entropy. The analysis of maximum hardness index indicates that only $Ag(PMe_3)_3$ is chemically unstable, while the stability of the rest compound satisfies the requirements of FEBID precursors. The low chemical stability of $Ag(PMe_3)_3$ indicates that this compound could not be used as a precursor for FEBID too.

The electronegativity, which characterizes the capacity of a compound to attract electrons from the compounds bonded with it, is used to compare toxicity of the compounds. It is well known that higher electronegativity indicates higher toxicity. It is necessary to mention that comparison of the Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3) electronegativity obtained with Pauling electronegativity of silver atom converted to eV allows conclude that the molecule under investigation is less toxic than silver atom, i.e. its toxicity is lower than that of Ag [13]. The electronegativity and, as a consequence, toxicity of $Ag(PMe_3)_n$ (n=2,3,4) is smaller than that of Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe_3) (Table 1). It is the other reasons why the molecules could be the preferred choice of the precursor for FEBID.

The appearance energy of the Ag derivatives is a very important requirement, too. This energy could not exceed the energy of FEBID. For FEBID, the relevant energy range is 1 meV (slowed-down secondary electrons) and up to the keV regime (typical primary electron regime, forward and backscattered electrons) [14]. Let us remind that we investigated various dissociation processes occurring under low electron impact. The most promising processes are selected by using two criteria: the appearance energy of pure silver is the lowest; the process is initiated by one electron. The total number of processes investigated is ~ 40.

The most probable dissociation processes of $Ag(PMe_3)_2$ are presented in Table 2. The processes of the cation formation are selected taking into account the fact that the first ionization potential calculated is equal to 5.35 eV. The results obtained prove that the dissociation of $Ag(PMe_3)_2$ to Ag^{-1} and neutral PMe_3 could be more probable. The appearance energy of this process is equal to 0.69 eV and it occurs due to one electron impact (Table 2).

Table 2. The most promising dissociation reactions of $Ag(PMe_3)_2$ and the appearance energy of Ag during them.

Dissociation processes	Energy of appearance, eV
$Ag(PMe_3)_2+e \rightarrow Ag^0+2PMe_3^0+e$	1.387
$Ag(PMe_3)_2+e \rightarrow Ag^0+PMe_3^0+PMe_3^{-1}$	1.589
$Ag(PMe_3)_2+e \rightarrow Ag^{+1}+2PMe_3^0+2e$	8.191
$Ag(PMe_3)_2+e \rightarrow Ag^{+1}+PMe_3^0+PMe_3^{-1}+e$	8.393
$Ag(PMe_3)_2+e \rightarrow Ag^{-1}+2PMe_3^0$	0.692
$Ag(PMe_3)_2+e \rightarrow Ag^{+1}+PMe_3^0 + PMe_3^{+1}+ 3e$	14.370
$Ag(PMe_3)_2+e \rightarrow Ag^0+PMe_3^0 + PMe_3^{+1}+2e$	7.566
$Ag(PMe_3)_2+e \rightarrow Ag^{-1}+PMe_3^0 + PMe_3^{+1}+e$	6.871
$Ag(PMe_3)_2+2e \rightarrow Ag^{-1}+PMe_3^0 + PMe_3^{-1}$	0.893

However, it is necessary to note that the appearance energy of $Ag(PMe_3)$ fragment could be similar to that of Ag. For example, the appearance energy of $AgPMe_3$ and PMe_3 anion is equal to 0.853 eV, only ~0.1 eV is larger than that of the appearance of Ag anion and neutral PMe_3 fragments; the appearance energy of neutral Ag, positively charged and neutral PMe_3 or $AgPMe_3$ and neutral PMe_3 equal to 7.6 eV. It indicates formation possibility of a pollutant into deposit.

The results of investigation of $Ag(PMe_3)_3$ indicate that the derivatives are not acceptable as precursor for FEBID due to low chemical and thermal stability. The analysis of the appearance energy leads to this conclusion too. The results obtained indicate that Ag and three PMe_3 molecules or various its derivatives prefer to be separate, i.e. the total energy of $Ag(PMe_3)_3$ is higher than the sum of the total energies of its separate fragments.

The fragmentation of $Ag(PMe_3)_4$ is different from that of $Ag(PMe_3)_2$ due to steric hindrance. The appearance energy of Ag due to fragmentation of $Ag(PMe_3)_4$ is larger than that of $Ag(PMe_3)_2$. Hence, in the case of this derivative the cascade processes could occur for the Ag deposition, i.e. the deposition process could be more complicated than in the case of $Ag(PMe_3)_2$.

Referring to the results presented in Table 2 it is obvious that the appearance energy of Ag lies in the relevant energy range for FEBID. Purely empirically, it turns out that the purity of deposition process and post deposition treatments are dependent on the energy range of FEBID but it is out of the scope of the paper. We would like to emphasize that only in [3÷5] eV−energy range for FEBID difficulties to separate pure metal atoms and ligands could arise and effectiveness of deposition could be low. This is because of possible production of both charged and uncharged Ag atoms in this energy range. Hence, referring to results obtained, we may conclude that $Ag((PMe_3)_2$ could be used as a precursor for FEBID.

4. Conclusions

Referring to the results obtained, we may conclude that $Ag(PMe_3)_2$ and $(Ag(PMe_3)_4$ satisfy the main requirements of the stability and toxicity for the precursors of FEBID. However, the usage of $Ag(PMe_3)_4$ could be complicated due to cascade processes that allow predict the low purity of deposit. $Ag(PMe_3)_3$ could not be used as a precursor because of low thermal and chemical stability. The main ways of Ag appearance, as final results of $Ag(PMe_3)_2$, fragmentation under low electron impact, are suggested too.

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