SECTION 2. COMPUTATIONAL MECHANICS AND COMPUTER-AIDED DESIGN. HIGH-PERFORMANCE AND CLUSTER SOLUTIONS FOR COMPLEX SYSTEMS SIMULATION

AB INITIO STUDIES OF SILVER PRECURSOR FOR FEBID: $Ag(PMe_3)_2$ AND $Ag(PMe_3)_3$ DERIVATIVES

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I. INTRODUCTION

Currently, the investigation of magnetic nanostructures are one of the most active topic in condensed-matter and materials-science research, offering many opportunities [1]. The magnetic nanostructures could be applied for instance 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 of magnetic nanostructures are designed by various technique 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 tis 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, at will, 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 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 follow from the choice of the precursor molecule are follows in: 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 pump out of precursor molecules after use and possible contamination of the system [6].

The aim of our study is to determine the properties of $Ag(PMe_3)_2$, $Ag(PMe_3)_4$ and $Ag(PMe_3)_3$ aiming to suggest a new Ag precursor for FEBID. We investigate thermal and chemical stability, toxicity and the energy of the appearance 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].

II. 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 optimization results accuracy. The zero-point energy was included in the evaluation of the energy of appearance. 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 ionization potential and electron affinity. The ionization potential and affinity were calculated as difference of energies of ionized and neutral molecules.

The Gaussian program packages were applied here [9].

III. RESULTS AND DISCUSSIONS

One of the requirements of the precursor is their thermal stability [6]. It implies that derivatives are stable (preferable in 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 value of the binding energy per atom of Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe$_3$), which is stable in to air, is smaller than that of other derivatives investigated. It leads to conclusion that the thermal stability of Ag(PMe$_3$)$_2$ and Ag(PMe$_3$)$_4$ are higher than the rest derivatives. The lowest thermal stability is Ag(PMe$_3$)$_3$.

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(PMe3)2	6.88	1.79	1.55	0.32	0.79	1.08
Ag(PMe3)3	4.43	1.17	0.59	0.85	-0.45	1.17
Ag(PMe3)4	7.53	0.65	1.02	0.33	0.78	1.53
Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe3)	6.27	4.88	3.65	0.13	0.97	3.73

Referring to I Utke and 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 chemically stable. The values of hardness and softness, presented in Table 1, indicate high chemical stability of the, Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe$_3$) what coincide with results presented in [10] and indicate reliability of the approach applied. However, the chemical stability of Ag(PMe3)n (n=2,3,4) are lower than that of Ag(1,1,1,5,5,5 hexafluoropentanedionato)(PMe$_3$), what indicates the comparison of the values of chemical hardness, softness an HOMO-LUMO gap. These data are not enough to make conclusion on the chemical stability of Ag(PMe$_3$)$_n$ (n=2,3,4) because there is no evidence that these compounds are unstable. Hence, the maximum hardness index Y was calculated, too, as follows:

$$Y = 1 - 2S^2$$

It is exhibited that hard-hard binding frame is preferred in molecules which Y holds values over 0.5 [11]. The chemical bond can be still formed as the soft-soft combination in the molecules what Y stands bellow 0.5 values, however, with positive nonzero figures. Only negative values of Y indicate anti-bonding character that can further be associated to an anti-binding entropy. The result of the analysis of maximum hardness index indicates that only Ag(PMe$_3$)$_3$ are chemically unstable, while this stability of the rest compound satisfies the requirements of FEBID precursors. 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 allow us to conclude that the molecule under investigation is less toxic that silver atom, i.e. their toxicity is lower than Ag [12]. The electronegativity and, as 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 other reasons why the molecules could be the preferred choice of precursor for FEBID.

IV. CONCLUSION

Referring to results obtained, we may conclude that $Ag(PMe_3)_2$ and $(Ag(PMe_3)_4$ satisfying the main requirements of the stability and toxicity could be used as precursors for FEBID. $Ag(PMe_3)_3$ could not be used as precursor because of low chemical stability

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GEOMETRIC MODELING OF MIDI-FULLERENE GROWTH FROM C_{40} TO C_{68}

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I. INTRODUCTION

Most investigations of fullerenes have centered on either obtaining these materials experimentally or studying properties of the materials which structure was known before. Are there fullerenes smaller than C_{60} and other than known ones which are stable enough to be discovered? The comprehensive experimental study on small or middle-size fullerenes revealed the following [1]. In the mass spectra of products of benzene pyrolysis, the authors found out the ions of all kinds of carbon molecules including small carbon molecules (C_3-C_{20}) and "quasi-fullerenes" C_{21}, C_{23}, C_{33}, C_{48}, C_{52}, C_{54}, C_{56} and C_{58}. (We conserve here the terminology by the authors). However, up to now the structure of these molecules is unknown. To our mind, the crucial questions for advanced applications of these materials are: how the materials are originated, what structure they obtain during growth, and how to classify them. Answer to these questions gives the possibility to develop nanotechnology on a scientific basis.

Numerous theoretical calculations have been performed for smaller fullerenes which structure was postulated by the founding fathers, mainly by H.W. Kroto [2]. However, it should be realized that "Man proposes, God disposes", so even the postulates by famous scientists do not give a guarantee of predicting all the possible structures. We claim that the geometric modeling in combination with the graph theory [3-5] allows not only to postulate a possible way of forming and growing carbon clusters (Man proposes), but to receive their structure automatically. It should be emphasized that the final structure obtained is unknown beforehand and mostly is unexpected for a researcher (God disposes).

Using such approach and taking as a basis different mini-fullerenes, we have designed various families of midi-fullerenes [4] and have carefully studied Endo-Kroto mechanism of growing fullerenes [5-7], according to which a carbon dimer embeds into a hexagon of an initial fullerene. In this case there arises a new atomic configuration and there is mass increase of two carbon atoms. Modeling the growth of fullerenes originating from fullerene C_{24} (D_{3h} symmetry), we have obtained the perfect fullerenes C_{30} and C_{36}