JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 11-12 , November – December 2011, p. 1450 - 1453

Nanocarbon embedded chalcogenides. Onion-like model

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We modeled the equilibrium structure, at 0 K temperature, of some spherical As_2S_3 molecules with only 12 rings of ten member (alternating As and S atoms) and 20 triangular faces: $As_{60}S_{90}$ (like C_{60}), $As_{140}S_{210}$ (like C_{140}), $As_{320}S_{480}$ (like C_{320}), grown on carbon fullerene and $As_{20}S_{30}$ (like C_{20}). We used a Monte-Carlo relaxation procedure in the frame of valence force fields theory. The onion-like configurations of the arsenic sulphide was demonstrated as possible. The deposited films of As_2S_3 seen in the cross-section prove the presence of onion-like configurations even in pure As_2S_3 material.

(Received November 1, 2011; accepted November 20, 2011)

Keywords: Chalcogenides, Nanocarbons, Onion-like configuration

1. Introduction

The structure of chalcogenides is still a subject of debate. Many papers have been published recently in this field [1-4]. In the last years a considerable attention was paid to some exotic structure able to be formed in two-dimensional configurations [5-9]. We tried in this paper to demonstrate that a multilayer arrangement of chalcogenide (As_2S_3) around the fullerene seed can be easily organized.

2. Computational method

The determination of the structure of new nanomaterials based on chalcogenide materials with nanocarbons was carried out by structural modelling assisted by computer. The minimization of the free energy of the models was performed in the frame of the theory of the valence force field. The total free energy of the clusters of atoms is the sum of the bonds stretching energy (E_{str}) and bonds bending energy (E_{bend}). There is included a simple analytical term for the Van der Waals energy of interaction. E_{str} was taken as $A(r^2 - r_0^2)^2$ with A = 86.7 meV/Å^4 and E_{bend} was taken as $B(\alpha-\alpha_0)^2$ with B = 24.03 meV/rad^2. The force constants A and B were approximated on the basis of Raman results published by Ludvig et al. [10] and Shastri et al. [11]. r_0 is the equilibrium bond distance (2.25 Å) and α_0 is the equilibrium bond angle (101.1º).

Firstly, the network of the atoms is created with a specialized program and the initial coordinates of the models are obtained. The total free energy is calculated. A Monte Carlo method is used for minimization of the total free energy of the model. Thereafter, the structural parameters of the model with minimum free energy is calculated in order to compare with the experimental structural data. The most important parameters are: the bond angle distribution, the distribution of the bond length and the radial distribution function.

3. Topology of the models

The topology of fullerene and fullerene like chalcogenide is represented in Figure 1 and 2.

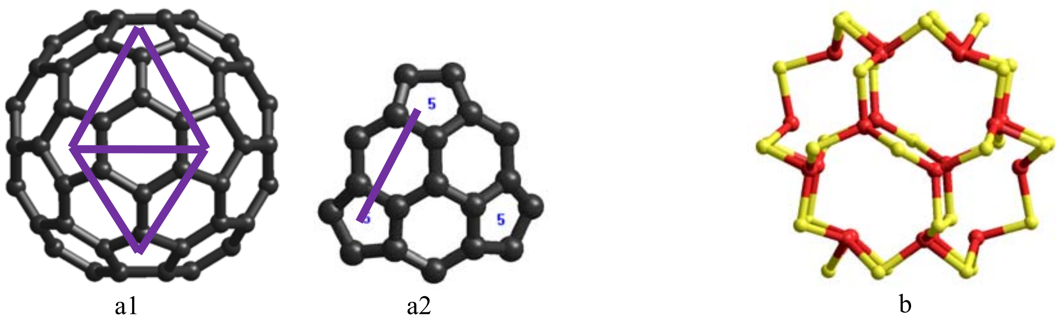

Fig. 1. The seeds of onion-like chalcogenide: a. Carbon fullerene C_{80} with 12 rings of 5 C atoms (a1) and 20 triangular faces (2,0) (in Coxeter notation) (a2).b. Fullerene-like chalcogenide $Ch_{20} = As_{20}S_{30}$, 12 rings of 10 atoms (alternating As and S atoms) and 20 triangular faces (1,0) (in Coxeter notation). $(E_{str}+ E_{bend})$ / at. = 0.497 meV

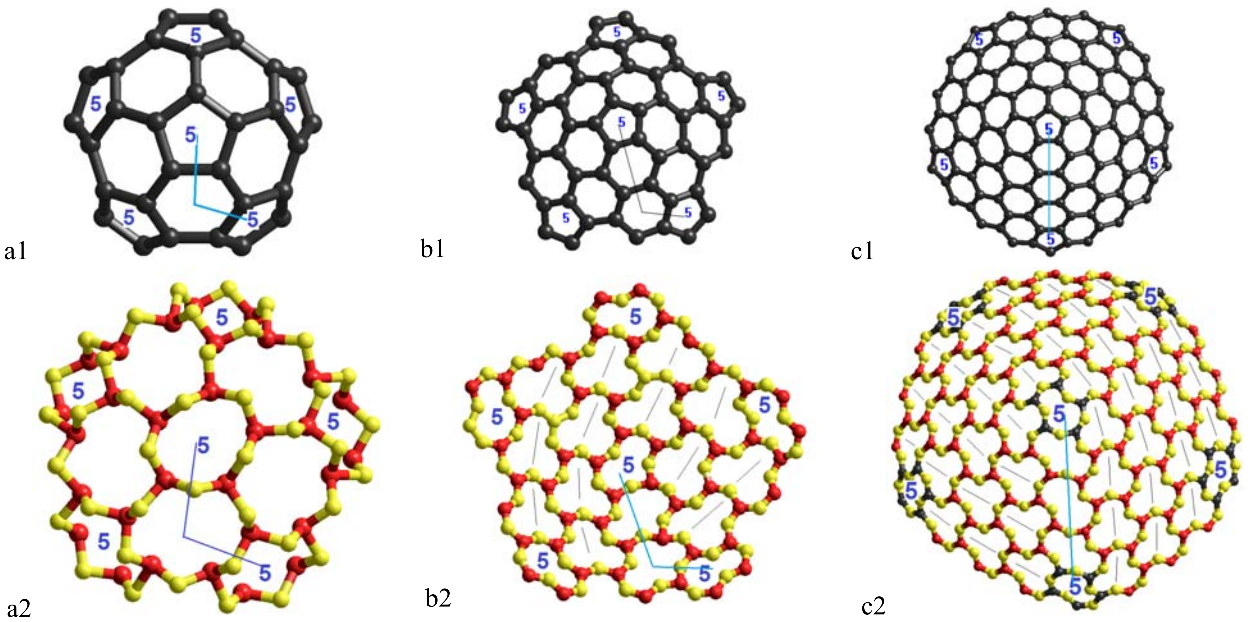

Fig. 2. Construction of fullerene-like chalcogenides $Ch_{60} = As_{60}S_{90}$ (a2), $Ch_{140} = As_{140}S_{210}$ (b2) and $Ch_{320} = As_{320}S_{480}$ (c2): As replace C in the network of C_{60} (a1), C_{140} (b1) and C_{320} (c1), S bonds As atoms.The fullerene-like chalcogenides show 12 rings of 10 atoms (alternating As and S atoms) and 20 triangular faces (in Coxeter notation): C_{60} and Ch_{60} show 20 triangular faces (1,1), C_{140} and Ch_{140} has 20 triangular faces (2,1), C_{320} and Ch_{320} has 20 triangular faces (4,0).

In Figs 2.b2 and 2.c2 it is shown the reason for the increase of the deformation bonds energy with cluster diameter: the presence of the 10-fold ring is equivalent to the sectioning of the planar crystalline layer of As_2S_3 and elimination of a sector of 60^o. Reinserting of the As_2S_3 layer leads to the curving of the structure and to stretching of the junction.

4. Results

The final models achieved after minimization of free energy of the structures are presented in Figures 3-5. We have built the first shell of the onion-like configuration: $Ch_{60} = As_{60}S_{90}$ and the largest fullerene which can be inserted into it has proved to be C_{80} (Fig 3a). We can deduce the radii of next shells of onion-like chalcogenides. Knowing the radius of carbon fullerene C_{80} (r_{C80}) and radius of chalcogenides fullerene Ch_{60} (r_{Ch60}) determine the ratio $\rho = r_{Ch60} / r_{C80} = 2.464$. Multiplying ρ to the known radius of other carbon fullerenes we get the desired radius of other chalcogenides fullerenes of the same topology, so the van der Waals distance between two adjacent fullerene to be that known for crystalline As_2S_3: 4.8 Å. The second shell was assumed to be Ch_{140} (Fig. 3b). The third shell was assumed to be Ch_{320} (Fig. 4, 5).

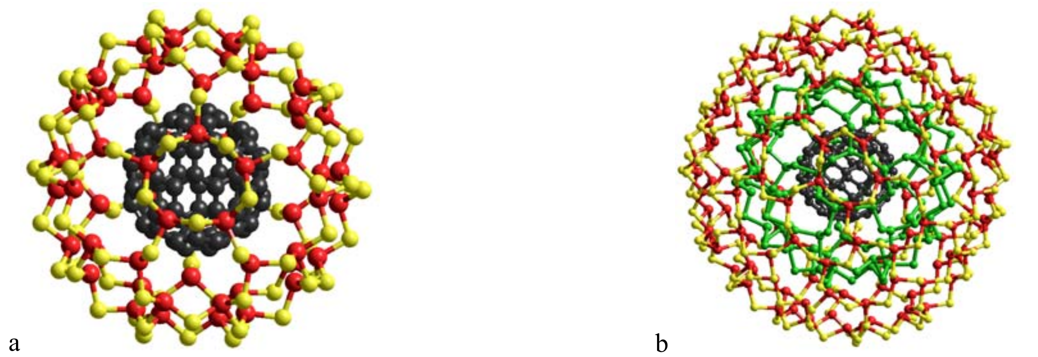

Fig. 3. a. C_{80} embeded in fullerene-like chalcogenide $Ch_{60} = As_{60}S_{90}$, $D_{internal}$ = 1.71 nm, $distance_{C80\text{-}Ch150}$ = 0.48 nm, $(E_{str}+ E_{bend})$ / at. = 0.002 meV, mean bonding angle: $<\theta>_{bonding}$ = 101.05^o and rms deviation from this value is $\beta = 0.65^o$. b. Onion-like chalcogenide (Ch_{60} and Ch_{140}) grown on C_{80}, $(E_{str}+ E_{bend})$ / at. = 0.035 meV, mean bonding angle: $<\theta>_{bonding}$ = 101.4^o and rms deviation from this value is $\beta = 1.6^o$. Only Ch_{60}: $(E_{str}+ E_{bend})$ / at = 0.029 meV. Only Ch_{140}: $(E_{str}+ E_{bend})$ / at. = 0.037 meV.

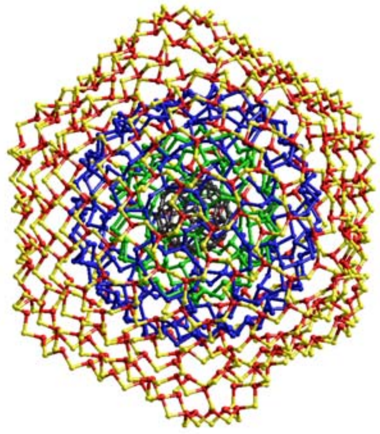

Fig. 4. Onion-like chalcogenide (Ch_{60} + Ch_{140} + Ch_{320}) grown on C_{80}. (E_{str}+ E_{bend}) / at. = 0.064 meV,
<θ>$_{bonding}$ = 101.3°, β = 2.3°
Only Ch_{60}: (E_{str} + E_{bend}) / at. = 0.046 meV.
Only Ch_{140}: (E_{str} + E_{bend}) / at. = 0.060 meV.
Only Ch_{320}: (E_{str} + E_{bend}) / at. = 0.076 meV.

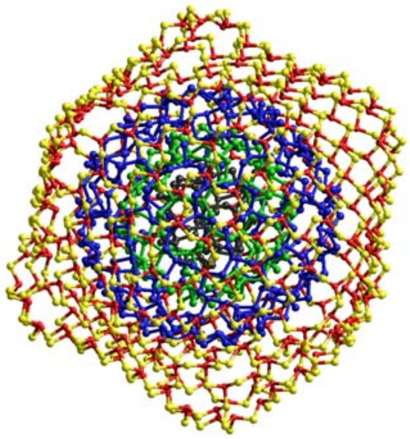

Fig. 5. Onion-like chalcogenide (Ch_{20} + Ch_{60} + Ch_{140} + Ch_{320}).
(E_{str}+ E_{bend}) / at. = 0.068 meV,
<θ>$_{bonding}$ = 101.4°, β = 2.25°
Only Ch_{20}: (E_{str} + E_{bend}) / at. = 0.559 meV.
Only Ch_{60}: (E_{str} + E_{bend}) / at. = 0.011 meV.
Only Ch_{140}: (E_{str} + E_{bend}) / at. = 0.044 meV.
Only Ch_{320}: (E_{str} + E_{bend}) / at. = 0.059 meV.
The outer diameter of Ch_{320} = 45 Å

5. Discussion

The onion-like structure has been suggested to occur in chalcogenide materials (Fig. 6). The arsenic sulphide has been deposited by thermal evaporation method. Sections of the films of As_2S_3 were prepared. One observes in the SEM microscope picture (Fig. 6) some round configurations to be ascribed to onion-like configuration in the material.

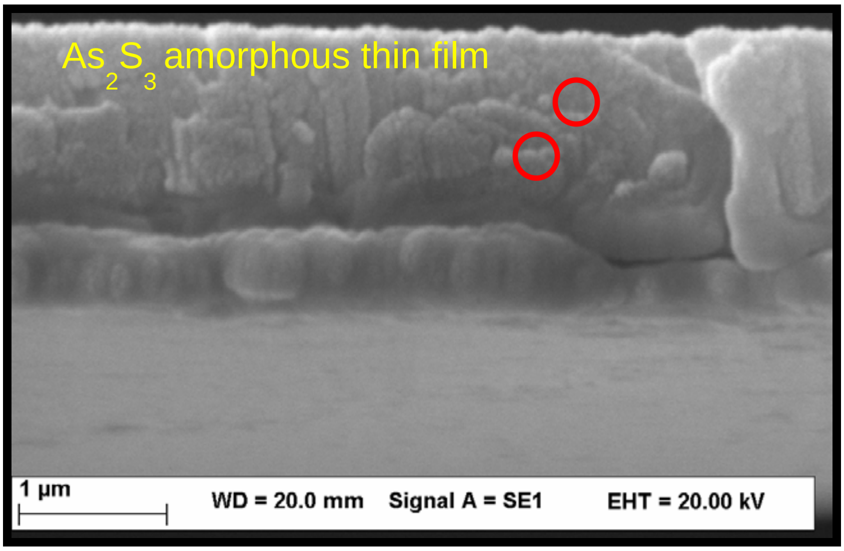

Fig. 6. Possible experimental evidence of onion-like chalcogenide in SEM picture.

6. Conclusions

We have demonstrated that onion-like chalcogenide can be built with correct bond distances and correct bonding angles known from the crystalline components of As_2S_3.

Using carbon fullerenes increases the probability to obtain regular shapes of onion-like chalcogenides.

An important feature of the model of onion-like chalcogenide is the absence of the dangling bonds and the lack of valence alternation pairs (VAP) defects.

Acknowledgement

This work was supported by CNCSIS – UEFISCDI (Romania), project number PNII - IDEI 1356 / 2009 (Contract IDEI No. 709 / 2009).

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