Ab initio modeling of carbon films deposited by laser plasma

V V Ilyasov, O M Holodova, I V Ershov, N V Prutsakova, T P Zhdanova, I P Gritsay and A V Ashkanov

Department of Physics, Don state technical university, 344000, Gagarin Square 1, Rostov-on-Don, Russia

E-mail: viily@mail.ru

Abstract. The results of modeling of atomic and electronic structures of amorphous ultrathin carbon films are presented from the first principles. The calculations of the system total energy were performed within the density functional theory using the Grimme DFT-D2 scheme. The atomic models of amorphous carbon films of a-C and a-C:H types are proposed. The calculated electronic energy spectra of the amorphous carbon films a-C:H models are well consistent with UPS and XANES of graphite and the hydrogenated carbon film. On the basis of DFT calculation the energy gaps for the considered models of amorphous carbon a-C:H are determined and the mechanisms of its formation are discussed.

1. Introduction
The amorphous carbon unique properties (mechanical durability, transparency in a wide range of spectrum, chemical inertness) open up the prospects of its use in the elements of optical and nanoelectronics devices [1, 2]. The ultrathin films of amorphous carbon a-C (:H) have metastable structure which is formed by mixing of fractions with the sp$^3$ - and sp$^2$ - carbon atomic binding. Within J. Robertson’s [3] model the lattice sites with an sp$^3$-binding are put into the clusters with a graphite-like sp$^2$ - binding. The hydrogen content up to 60% is noted in the films a-C (:H). The ratio sp$^3$/sp$^2$ in the hydrogenated carbon films depends on the technological conditions of their synthesis and the choice of a coating process method. In addition, this ratio correlates with the value of the optical gap in the amorphous carbon a-C (:H) energy spectrum.

In this paper, the simulation of atomic and electronic structures of amorphous ultrathin carbon films a-C(:H) synthesized by pulsed laser deposition (PLD) is performed from the first principles. The simulation was performed based on the density functional theory (DFT).

2. Model and method
In DFT calculation the simplest atomic models of ultrathin films of the a-C and a-C:H types: graphene, (graphene, G) and single-side-hydrogenated graphene, SSHG are used. It is known, that in hexagonal graphite structure the interaction between the carbon layers in the direction [0001] is slight (insignificant). The latter allows us to construct a model atomic structure, using, for example, four graphene layers in the Bernal’s (ABAB) laying. The quasi-two-dimensional models of the a-C and a-C:H types films are constructed according to the slab scheme. Each slab has been separated from the other with the vacuum area in the direction (0001) of 1.5 nm. The supercell fragments presented in
The atomic structure of the hydrogenated carbon model is formed by 4 graphene nanosheets and 2 hydrogen monolayers. DFT calculations of total energy of these systems have shown that these configurations are the most stable. The supercells include graphene unit cells (4x4) in the plane (0001).

The total energy and the system electronic spectrum are calculated by the pseudopotential method within the density functional theory (DFT) similar to works [5, 6]. In particular, nonlocal exchange and correlation functional in parametrization of Perdew-Burke-Ernzerhof (PBE) has been used [7]. The plane wave cutoff energy of 410 eV was used for the self-consistent calculation. The convergence of a cell total energy not less than $10^5$ Ry/cell is achieved. The functional with the dispersion correction (PBE-D2) [8] is used for the van der Waals interaction accounting.

**Figure 1.** The amorphous carbon film fragments: side view (a) a-C type and (b) the a-C:H type (after relaxation). Top view (c). Carbon atoms (yellow) and hydrogen (turquoise).

### 3. Results and discussion

Based on the DFT the a-C model, formed by 4 graphene monolayers, atomic structure has been studied. The vertical distance between the monolayers was 0.335 nm. In the graphene layers, the C-C bond length was 0.142 nm. The atomic structure relaxation of a-C model film has been performed. TDOS and partial (PDOS) electronic state densities are calculated for the noted atomic model of amorphous carbon films a-C. In figure 2 TDOS and PDOS of ultrathin a-C films are correlated with a ultraviolet photoelectron spectrum UPS and the near-edge XANES area of pyrolitic graphite. The combination of TDOS and UPS and XANES spectra was performed by the main maxima with energy-6.9 eV and 1.9 eV. It should be noted that the calculated electronic energy spectrum (TDOS) of the offered above model of the amorphous carbon film a-C is well consistent with the graphite spectra UPS [9] and graphite XANES [10] (see figure 2).

In figure 2 projected electronic density on 2s- and 2p-states of carbon are given. PDOS analysis allows to note, that the vicinity of the Fermi level in the energy range from $-5$ eV to $+5$ the eV is formed by the filled and free states of carbon 2p-electrons. The valence electron C2s-states are in the energy range ($-20_{-6}$) eV. Thus, the bonding and antibonding states of the carbon C2p-electron states form the energy gap with the value $E_g = 0.4$ eV at the Fermi level. This value is 1.5 times less than that of the data of the theoretical calculation for graphite, which was made by the authors [11]. The obtained energy gap estimation characterizes the 4 graphene sheets model in which there is an interaction between graphene layers. The weak symmetry violation of sublattices in the carbon monolayers may be responsible for this interaction similar to the graphene bilayer (BLG) [12, 13]. The BLG energy spectrum has the gap $E_g = 0.1$ eV the value of which is measured by the infrared spectroscopy method [13].

The atomic structure of the hydrogenated carbon model a-C:H is formed by 4 graphene nanosheets and 2 hydrogen monolayers (see figure 1(b)). The C-H bond length initially was 0.111 nm. As a result of the atomic structure relaxation, the length of C-H-bond was 0.116 nm. The equilibrium lattice parameters, the atomic positions of the atoms of 4 graphene nanosheets and 2 hydrogen monolayers, the vertical distance between graphene atomic layers and the C-C - bond length in the plane (0001) are determined. The vertical distance between the interior monolayers was 0.320 nm, and as a result of
relaxation, the external graphene monolayers moved at a distance 0.313 nm from the interior sheets. The C-C length - bonds in the graphene internal layers was 0.142 nm, and it was 0.146 nm in the external (outer) sheets. The later indicates the C-C bond deformation. For the above considered atomic model of amorphous carbon a-C:H type films, the total (TDOS) and partial (PDOS) density of electronic states were calculated. PDOS are calculated in the spin-polarized variant.

Figure 2. DFT calculation of TDOS and projected s- and p-DOS of the amorphous carbon a-C film in comparison with UPS [9] and XANES [10] spectra of the a-C film.

Figure 3. Total density of states TDOS (blue) in comparison with the UPS [9] and XANES [10] spectra (top panel) and projected on atomic orbitals DOS (per atom) for a-C:H - C2p (blue), C2s (red), H1s (purple) - bottom panel.
In figure 3 total DOS of the a-C:H model which is compared with the ultraviolet photoelectron spectrum UPS and the near-edge XANES spectrum of the a-C:H carbon film is shown. The overlapping of TDOS and UPS and XANES spectrum was performed by the main maxima with energy -6.8 eV and 1.9 eV. It should be noted, that the calculated electronic energy spectrum (TDOS) of the considered above amorphous hydrogenated carbon a-C:H model, is qualitatively consistent with the UPS [9] and XANES [10] spectra of the hydrogenated carbon a-C:H (see figure 3). The difference of the theoretical and experimental spectra is the existence of two peaks with the energy -0.9 eV and 1.9 eV, which are located on the Fermi level both sides, in the calculated electron energy spectrum. The existence of these peaks is caused by the rearrangement of the electronic structures at the hydrogenation of the upper and lower graphene monolayers. The peak 0.9 eV is determined by the electronic subsystem with a spin up, and the electron subsystem with a spin down is responsible for a peak with the energy 1.9 eV. In the a-C:H system, the Fermi level energy gap $E_g = 0.2$ eV is formed by the bonding and antibonding states of carbon C2p-electrons.

4. Conclusions
Based on the density functional theory (DFT), the modeling of the amorphous carbon a-C and the a-C:(H) films deposited by laser plasma is performed. The calculated electron energy spectra of model amorphous carbon films of a-C (: H) are well consistent with UPS and XANES of graphite and the hydrogenated carbon film. The energy gaps for the model amorphous a-C(:H) carbon films are defined.

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