International Conference on Renewable Energies and Power Quality (ICREPQ'17)
Malaga (Spain), 4th to 6th April, 2017
Renewable Energy and Power Quality Journal (RE&PQJ)
ISSN 2172-038 X, No.15 April 2017

Functionalized Graphene and Hexagonal Boron Nitride (hBN) Two-Dimensional Heterosystems for Solar Cell Applications

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ABSTRACT: We present preliminary results of theoretical investigation of mono- and multi-layers of graphene (G), hexagonal boron nitride (hBN) and/or their combinations, functionalized with hydrogen, which are prospective for photovoltaic (PV) applications. Controlled hydrogenation of the above layered systems allows to simultaneously tune 2D electron gap of the materials, create strong covalent interlayer bonding or bond the multilayers to a substrate. The functionalized nanomaterials under investigation demonstrate not only chemical stability and natural hardness, but they are also compatible with standard growth technologies used in photovoltaics. Such multilayers can be used as transparent solar cell windows, an interfacial layer, *e.g.*, in a form of a tunnel junction, an electrode, 2D semiconducting material and other. In particular, graphene/hBN heterosystems considered, allow tailoring of structural, electronic and bonding properties by controlled dose of hydrogen. Their promising PV applications as well as already existing experimental implementations will be discussed in the end.

Key words: graphene, hexagonal boron nitride, hydrogenated multilayers, photovoltaic cells; transparent materials

1. Introduction

Recently we witness integration of different layers of two-dimensional materials for much wider applications than previously thought, including renewable energy such as, *e.g.*, photovoltaics [1,2], hydrogen storage [3] and other. The one-atom-thick 2D structures and/or their multilayers offer remarkable physical and chemical properties, which can make a profound impact in many areas of renewable energy. For instance, ubiquitous components of solar cell design are thin transparent films, thin tunnel junctions in tandem systems and other. To be successfully applicable in photovoltaics, a possibility of tailoring films properties, such as the band gap, ability to strongly bond with a substrate, stability and durability are mandatory. Among a variety of atom thick nano-layers, discovered after graphene has been experimentally prepared (see, *e.g.*, [4] and refs. therein), 2D graphene and hexagonal boron nitride (hBN) are among the hardest and most chemically stable materials. Graphene and hBN have many properties in common, such as atomic structure, high mechanical strength, transparency, non-solubility in liquid water, relatively high room temperature thermal conductivity, *etc*. The disadvantages of these two materials include a weak van der Waals interaction with each other and neighboring materials (such as, *e.g.*, a substrate), while their electron gaps are not suited well for many PV applications: hBN is an insulator with too high (~ 6 eV) electron band gap, whereas graphene (also called here "G") is a semi-metal with a zero band gap.

In the presentation we will discuss how to overcome the above mentioned drawbacks of the graphene/hBN multilayers using controlled hydrogenation. After briefly reviewing recent applications of 2D nanofilms in photovoltaics, we consider various and promising 2D multilayer systems, functionalized by hydrogen. Such materials can enhance various characteristics of the solar cells, that influence their efficiency, stabilty and other. Possible implementations as solar cells componenets will be offered in the end.

2. Technical details and results

Density Functional Theory (DFT) within the Local Density Approximation (LDA) plane-waves and pseudopotentials scheme within the repeated slab geometry with 60 Ry cutoff have been used in the simulations of the structure, bonding and dynamics. The geometry optimization is achieved through the relaxation of the structure toward its total energy minimum. Finite temperature molecular dynamics (MD) was also used (i) to check whether the hy-

drogenated multilayer systems are structurally stable with respect to the thermal annealing and (ii) to extract the vibrational frequencies, also required for noninvasive systems characterization. The possible structural instability is indicated by an appearance of the soft phonon mode in the vibrational spectra. Electron band structure, density of states (DOS), vibrational DOS (VDOS), linear and nonlinear optical response, calculated for selected configurations, will be presented. The optical response is important for *in-situ* spectroscopy of the materials. For more numerical details, see, *e.g*., [5]. For the most promising systems very accurate calculations of the linear dielectric function, which include many-body corrections, have been carried out. The technical details of the many-body formalism used can be found in [6].

Out of 40 different 2D bilayers, trilayers and more complex multilayer systems considered, we discuss here the most interesting: (i) G/hBN bilayer, passivated by hydrogen on both sides of the bilayer with maximum hydrogen coverage, equal to 50% of monolayer (complete hydrogenation, see Fig. 1, side and top views), as well as partially hydrogenated bilayers (not shown here). (ii) Other systems to be discussed include the hydrogenated G-BN-G and BN-G-BN trilayer, (iii) completely and partially hydrogenated at both sides bilayers of graphene with C – C interlayer covalent bonds. (iv) Finally, considering the importance of having well bonded top layers for, *e.g.*, transparent solar cell windows, it is proven that partially hydrogenated at the top multilayer system can form strong covalent bonding with the substrates.

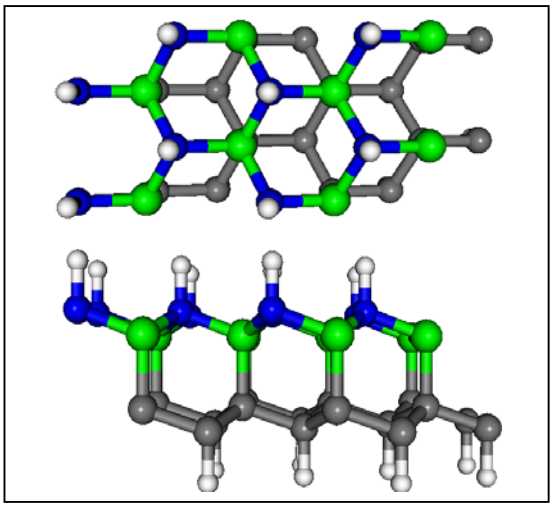

Fig. 1. Most energetically stable graphene/hBN 2D heterosystem, 50% hydrogenated at both sides with AB stacking: the top view (at the top) and the side view (at the bottom). Atoms are shown as: H – white, C – grey, B – green, and N – blue balls.

Important to stress is that the covalent bond formation is also responsible for substantial modification of the electron band structure in the hydrogenated heterosystems, compared to pristine multilayers. In agreement with the well-known results, our calculations show that the pristine graphene is gapless, while the calculated DFT LDA gap of hBN is 4.1 eV. However, 50% hydrogenated AB stacked 2D heterostructure (Fig. 1) demonstrates DFT-LDA energy gap of 1.1 eV. On the other hand, in marginally higher in the total energy AA stacked heterosystem a slightly lower energy gap of 1.0 eV is opened, as it is shown in Fig. 2.

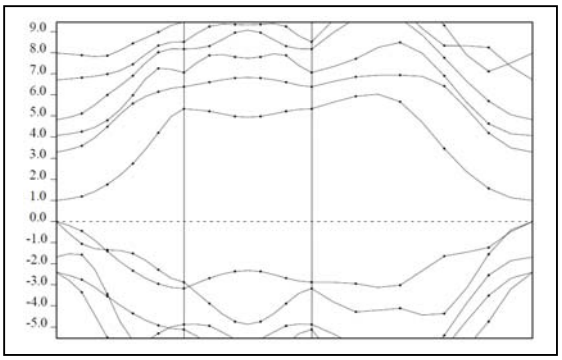

Fig. 2. Electron band structure of completely hydrogenated G/hBN AA stacked bilayer. Direct DFT LDA gap of 1.0 eV is located at Γ. AB stacked bilayer demonstrates very similar bands with slightly higher gap of 1.1 eV.

Important to stress that the AA staked heterosystem (as well as AB stacked one) opens the direct gap. Such direct gap is important for numerous optical applications.

Considering DFT-LDA underestimation of the energy gap, formation of the 50% hydrogenated 2D bilayer should cause in experiment the electron energy gap opening to about 1.5 eV (calculations of the many-body corrections to the band gap and the strong excitonic effects are in progress). This is close to the optimal gap value for PV and other microelectronics applications. Furthermore, our many-body correction results indicate that there is a prominent excitonic peak (*e.g.,* at 2.2 eV for the G/hBN bilayer, shown in Fig. 1), which depends on the system and hydrogen content. This peak, such as other spectral peculiarities could serve as an optical signature of the structure and the hydrogen dose, thus enabling in-situ optical characterisation of the 2D materials considered during the growth procedure or incorporated into the PV devices.

When reducing the hydrogen dose at both sides of the bilayer, for instance, to 25% (twice less than the maximum possible coverage of 50%) a more complex structure is formed. Important is that reduction of the hydrogen coverage causes a decrease in the energy gap for this structure: its DFT-LDA value is 0.2 eV. This clearly demonstrates that the partial hydrogenation enables 2D electron band energy gap engineering, important for PV. Experimentally, the hydrogen adsorption below the maximum coverage is a random process, which forms non-periodic 2D hydrogenation pattern. Even though we did not carry out more complex and CPU demanding modeling of such random system, we should expect the monotonous increase of the gap with higher H coverage. Indeed, our theoretical finding of the possibility of the gap tailoring in partially hydrogenated graphene [5] has been experimentally proven independently.

Examples of more complex and also interesting heterosystems, such as 50% hydrogenated G/hBN/G trilayer and

50% hydrogenated graphene layer *covalently* bonded to cubic BN substrate are also considered. Hydrogenated trilayer heterosystem demonstrates 0.8 eV DFT LDA gap. For such a system expected experimental gap should be close to 1.4 eV, comparable, *e.g*., to that one of GaAs. Finally, the low H dose functionalised graphene on top of a substrate can form 2D material with the intermediate band gap, another important concept for implementation in PV.

To investigate the hydrogenated heterosystems' thermal stability we carried out the finite temperature MD simulations. In particular, the time dependent instantaneous MD temperature of the 50% hydrogenated AB stacked graphene/hBN bilayer (Fig. 1) has been carried out. It shows that the hydrogenated bilayer is thermally stable at the temperature up to 1500K. The corresponding vibrational frequencies has been extracted from the MD simulations, the spectra indicate not only thermal stability of the heterosystem, but the appearance of the strong interlayer covalent bonds. On the other hand, the extracted vibrational signatures offer interpretation of noninvasive infrared or Raman spectroscopy results. We have to stress that the above numerical test of the system stability is very important: several heterosystems considered in this study have demonstrated that their ground state structure is not preserved when the temperature reaches several hundred degrees, typical, *e.g.,* for the growth technology. Such instability is directly revealed by appearance of the so called soft phonon mode in the calculated vibrational spectra.

3. Summary

In conclusion, different physics concepts have been considered to improve the photovoltaics systems efficiency and stability, including applications of the nanomaterials such as nano-layers and quantum dots. Some of them have been already implemented or are in the active research phase. We have demonstrated that different 2D graphene-like systems, functionalised with hydrogen, can improve the overall performance of photovoltaic devices. Additionally, their characteristics can be efficiently monitored *in-situ* by optical or vibrational means by comparing experimental results with calculated responses, presented here. Use of such 2D system as an electrode, transparent top layer and an interfacial layer, such as tunnel junction in tandem solar cells will be beneficial for PV systems. Since the research on solar cells, containing in its design graphene-like nanolayers, are still at laboratory scale, more efforts have to be undertaken to extend their application to the industrial PV technology.

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