THEORETICAL INVESTIGATION OF GEOMETRY AND ELECTRONIC PROPERTIES OF C60 MOLECULE PLACED ON SI (001) AND SI (111) SURFACES

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Abstract — Atomic and electronic structure of C60 molecules deposited on Si (001) and Si (111) surfaces were investigated within the framework of density functional theory. Different configurations of compartments mutual arrangement were considered. Then, electronic structure of the most favorable ones was analyzed. It was found that silicon surfaces change their properties significantly due to the interaction with fullerene molecule. Fullerene, in turn, loses its high symmetry which also leads to change in electronic structure.

Index Terms — Buckminsterfullerene, Density Functional Theory, Silicon, Quantum Dots.

I. INTRODUCTION

Quantum nanodots (QD) are of a great interest due to their high potential for microelectronic, optoelectronic or thermoelectric applications and even for quantum computing. The most widely used in QD materials are semiconducting ones like silicon, metal silicides and hydrogen-capped silicon nanoparticles [1], [2]. However, large size distribution leads to difference in electronic and optical properties for these materials. That is why using equal-sized fullerenes as QD is highly desirable. Fullerenes possess unique mechanical properties, chemical inertness and interact with electromagnetic field effectively. Nevertheless, fullerene molecules should be isolated from each other which can be achieved by fixing them in matrix. Single layer of C84 fullerene embedded Si (111) surface was fabricated through a controlled self-assembly mechanism in an ultrahigh vacuum (UHV) chamber [3], [4]. It has a high emission efficiency and low turn-on voltage, which makes it very promising as a field emitter source. STM I-V measurement shows that the embedded C84 molecules have a wide band gap of ~3.4 eV. C60 molecules were successfully deposited on Si (001) surface forming flat thin film with thickness up to 25 nm [5]. Covering of silicon surface with C60 leads to significant decrease in friction coefficient. However, there are only few theoretical studies of fullerenes covering the silicon. Properties of C84 film were studied within DFT-LDA approach [4] but silicon substrate wasn’t taken into account due to limited computational resources.

In this article we have investigated atomic and electronic structure of C60 regularly deposited on Si (001) and Si (111) surfaces by means of density functional theory.

II. MODELS AND METHOD

All calculations were performed within the frame of density functional theory [6], [7] using VASP package [8], [9]. Projected augmented wave method (PAW) [10], [11] and PBE exchange-correlation functional [12] were implemented. The energy cutoff was set to 400 eV. Geometry optimization was carried out until forces acting on atoms were smaller than 0.05 eV/Å.

Fig. 1. C60 fullerenes atop reconstructed Si (001) surface: a — initial geometry; b — rotated geometry. Surface silicon atoms are denoted as big light grey balls.

Thickness of 12 atomic layers was found to be enough for reproducing the main features of both Si (001) and Si (111) surfaces. In order to avoid the
influence of dangling bonds, the 2×1 dimer surface reconstruction of Si (001) was simulated (see Fig. 1) whereas Si (111) slab was passivated with hydrogen atoms. The distance between two neighboring fullerenes as well as vacuum interval normal to the slab was set to ~10Å so they did not affect each other in periodic boundary conditions.

Two different possibilities of fullerene location on Si (001) surface were considered. One of them requires rotation by 90° relatively to Si dimers and another one doesn’t (see Fig. 1). The Monkhorst-Pack k-point Brillouin sampling [13] was implemented. K-point mesh contained 6×6×1 points. Three different positions of C_{60} on Si (111) can be suggested (see Fig. 2): a) 2 silicon atoms bound to 1 and 4 carbon atoms in fullerene hexagon (“hex” position); b) 2 silicon atoms bound 5 and 6 carbon atoms in fullerene hexagon (“bond” position); c) 3 silicon atoms bound to 2, 4 and 6 carbon atoms in fullerene hexagon (“trig” position). K-point mesh contained 3×3×1 points in each case. Binding energy for C_{60} molecule placed on silicon surface was calculated as:

\[ E_b = E_{\text{Si-fullerene}} - E_{\text{Si}} - E_{\text{fullerene}}, \]

where \( E_{\text{Si-fullerene}} \) and \( E_{\text{Si-fullerene}} \) are total energies of silicon surface, fullerene molecule and hybrid structure, respectively.

### III. RESULTS AND DISCUSSION

#### A. Modeling of C_{60} molecules on Si (001) surface

Calculated binding energies, which are -3.610 eV and -4.279 eV for original and rotated structure, correspondingly, show that the latter one is more likely to occur. Then, densities of states (DOS) for the most favorable structure were calculated.

Fig. 3 shows how DOSes of compartments change after formation of hybrid structure. It’s visible that C_{60} deposition on Si (001) surface leads to the breaking of dimers and surface amorphizing. High-symmetry peaks of fullerene are split due to the interaction with silicon.

#### B. Modeling of C_{60} molecules on Si (111) surface

The binding energies for “hex”, “bond” and “trig” configurations are -3.569, -2.930 and -2.752 eV correspondingly.

“Hex” configuration is then much more favorable than other ones. Total (DOS) and partial (PDOS) densities of states were plotted for this preferable structure. PDOSes of fullerene in hybrid C_{60}-Si(111) structure demonstrate features similar to those of C_{60}-Si(001). We can clearly see that silicon and fullerene molecule affect the electronic structure of each other. The interaction of buckminsterfullerene molecule with silicon surfaces was then found to be favorable and opening new possibilities of their utilization in nano- and optoelectronics. However, the present
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study is aimed to shed a light on surface interaction. Fullerene embedding into the silicon is to be investigated in future.

REFERENCES