The Adsorption Properties of the Diamond Surface (111)-2×1 with the Vacancy Defect: Quantum-Chemical Simulation

Ananina O.Yu.[1], Severina E.V.[1], Lvova N.A.[2]

[1]*Zaporizhzhya National University, Zaporizhzhya, Ukraine*
[2]*Federal State Bugetary Institution "Technological Institute for Superhard and Novel Carbon Materials", Troitsk, Russia*

The goal of this work is simulation of possible states of vacancy defects on the diamond C(111)-2×1 surface and the study of their electronic, geometric and adsorption characteristics. Simulation of graphenes was carried out by a group of methods: semi-empirical MNDO, PM3 and PM6 methods of MOPAC software, and also ab-initio Hartry-Fock methods of PC GAMESS program.

Searching of stable configurations of vacancy defects on a clean surface C(111)-2×1 leads to three states with different geometry, electronic properties, and energy of formation. The total system energy for the cluster in state 2 increases on 0.816 eV (ab initio) and 0.78 eV (semi-empirical) in comparison with that in state 1. In state 3 the total energy for the cluster is 0.272 eV (ab initio) and 0.1 eV (semi-empirical) higher than in the state 1. Formation of the vacancy defect does not lead to significant change in hybridization of carbon atoms orbitals: type of hybridization remains unchanged - sp^2+p, change occurs only with the value of s- and p-components of hybrid orbitals. There is no significant change in the charge distribution on the surface with the vacancy defects.

In this paper we have studied the adsorption of the hydrogen H_2 and water H_2O molecules on the C(111)-2×1 surface with the vacancy. Potential adsorption sites are the surface atoms in the chains with unsaturated bonds (involved in the formation of delocalized electron clouds) and atoms with the double bonds. During calculation have been estimated the values of energy characteristics of adsorption, such as the activation energy E_{act} of adsorption and binding energy (heat of adsorption, q). It was shown that the adsorption of the atomic hydrogen on the region of the vacancy defect have occurs without activation (E_{act}=0), unlike the adsorption on the ordered C(111)-2×1 surface wherein E_{act}=0.2÷0.45 eV.

The adsorption of H_2 and H_2O molecules occurs with the dissociation on the fragments. The chemisorption of hydrogen molecule $H_2 \leftrightarrow H+H$ requires the activation energy E_{act}=0,51 eV, which is much smaller than the binding energy in the H_2 molecule (E_b = 4.47 eV). For water molecules chemisorption by the mechanism $H_2O \leftrightarrow O+H_2$ need E_{act}=1,17 eV, and by the mechanism $H_2O \leftrightarrow OH+H$ the activation energy of adsorption is E_{act}=0,76 eV.

Thus, we can conclude that in the region of the vacancy defect on C(111)-2×1 surface having active adsorption centers which will affect the mechanism of adsorption and desorption of molecules and particles.