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Origin of piezoelectricity in monolayer halogenated graphane piezoelectrics

Hye Jung Kim [a], Mohammad Noor-A-Alam [a], Jong Yeog Son [b], Young-Han Shin [a,*]

[a] *Department of Physics and EHSRC, University of Ulsan, Ulsan 680-749, Republic of Korea*
[b] *Department of Applied Physics, College of Applied Science, Kyunghee University, Suwon 446-701, Republic of Korea*

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ABSTRACT

Periodic patterning with adatoms or defect is one of the methods for opening the band gap of graphene. In particular, under certain configurations controlled by the order of hydrogen and halogen atoms attached on graphene, inversion symmetry of graphene can be broken to give piezoelectricity as well as pyroelectricity. Using first-principles calculations, we examine the structural stability and electronic properties of four polar conformations of halogenated graphene $(C_2HX)_n$ to understand the origin of piezoelectricity in this two-dimensional system. The formation energies and piezoelectric coefficients manifest that the four conformations of $(C_2HF)_n$ are energetically stable with considerable piezoelectricity. We find that the electronic contribution of the proper piezoelectricity in $(C_2HF)_n$ is mainly related to the change of the electron distribution around F atoms. By substituting flourine with chlorine, we confirm that the piezoelectricity enhances at the expense of stability degradation.

1. Introduction

Since a single layer of graphene was successfully exfoliated from graphite [1], there have been a lot of researches in the physical properties and applications of graphene [2–8]. Graphene has strong carbon connection through sp^2 orbitals while the remaining p orbitals with delocalized electrons enables its excellent electron conductivity. No gap between the valence and conduction bands endows graphene with a special semimetal characteristic, and its electronic properties are depending on the position of the Fermi level [3].

The band gap opening of graphene is one of the crucial issues for the electronic application. Theoretical and experimental reports on graphene have shown that opening of the band gap at the Dirac points is possible by applying stress [5,6], attaching atoms in a patterned structure [4], or hybridizing graphene with hexagonal boron nitride [7,8]. Sofo et al. reported the possibility of graphane theoretically [9]. Afterwards the possibility of synthesizing partially hydrogenated graphene was experimentally verified [10]. Similarly, fluorinated graphite $(CF)_n$ was obtained by passing fluorine over graphite [11–14], and multilayer or monolayer fluorinated graphene was produced by mechanical or chemical exfoliation of the fluorinated graphite [13–16]. Piezoelectricity in graphene-based materials was recently reported by Ong et al. [17]. They showed that piezoelectric effects can be engineered into nonpiezoelectric graphene through the selective surface adsorption of atoms, such as H, F, Li, or K. Noor-A-Alam et al. showed that a single layer of hexogonal boron nitride had both in-plane and out-of-plane piezoelectricity if it was hydrogenated or fluorinated [18].

For piezoelectric materials, flexibility becomes one of the important roles to develop future soft devices in nanoscale due to the requirement of withstanding large amounts of strain to effectively change the mechanical energy into the electric energy, or vice versa. By using thin piezoelectrics in electric power production systems, it will be possible to increase the degree of integration as well as the efficiency of energy conversion in soft devices [19]. Because the thickness is inversely proportional to flexibility, it will be interesting to study the piezoelectricity of polar two-dimensional (2D) materials.

In this Letter, we examine the structural and electronic properties of several 2D fluorographane $(C_2HF)_n$ conformations [9,20] by using *ab initio* calculations performed within density-functional theory formalism. Since these 2D piezoelectric materials are topologically different from its possible one-dimensional analogue, polyvinylidene difluoride (PVDF), the transition between paraelectric and ferroelectric states will be intrinsically impossible due to the inappropriate dihedral rotation before the dissociation of C_2HF [21–24]. We measure the piezoelectricity of these 2D materials from the dipolar polarization change with respect to strain and stress. We also show that the piezoelectricity increases when the fluorine atoms are substituted with the more polarizable atoms such as chlorine, competing with the degradation of stability.

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* Corresponding author.
E-mail address: hoponpop@ulsan.ac.kr (Y.-H. Shin).

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2. Theoretical details

All calculations were performed within the framework of density functional theory as implemented in the Vienna Ab initio Simulation Package (VASP) [25]. The projector augmented wave method [26] was used with a cut-off energy of 500 eV. The exchange–correlation functional was given by a generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof parameterization [27]. Since band gaps within the GGA exchange–correlataion functional are known to be underestimated [28], we checked the band gap using the GW_0 approximation based on GGA wavefunctions and one-electron energies [29,30,28]. The Brillouin zone was divided by a 20×20×1 Monkhorst–Pack mesh [31] with its origin at the Γ point. Since periodic boundary conditions were applied in all three dimensions, a vacuum region of 19 Å and the dipole correction [32] in the normal direction were used to ignore the electric field due to the adjacent dipolar layers. Atomic positions were relaxed to find the lowest energy configuration with the conjugated gradient method until the force on each atom was smaller than 0.001 eV/Å.

3. Results and discussion

3.1. Stability and band structures

In this Letter, we consider only four simple dipolar conformations (chair, boat, zigzag, and armchair conformations) of $(C_2HF)_n$. Their schematic views and structural information are given in Figure 1 and Table 1. These conformations corresponds to the case where hydrogen atoms are attached from the top and fluorine atoms from the bottom of a graphene layer. In this case, carbon atoms are displaced along the normal direction from the plane of the graphene layer due to the attached H and F atoms interacting with the sp^3 orbitals of carbon atoms [9].

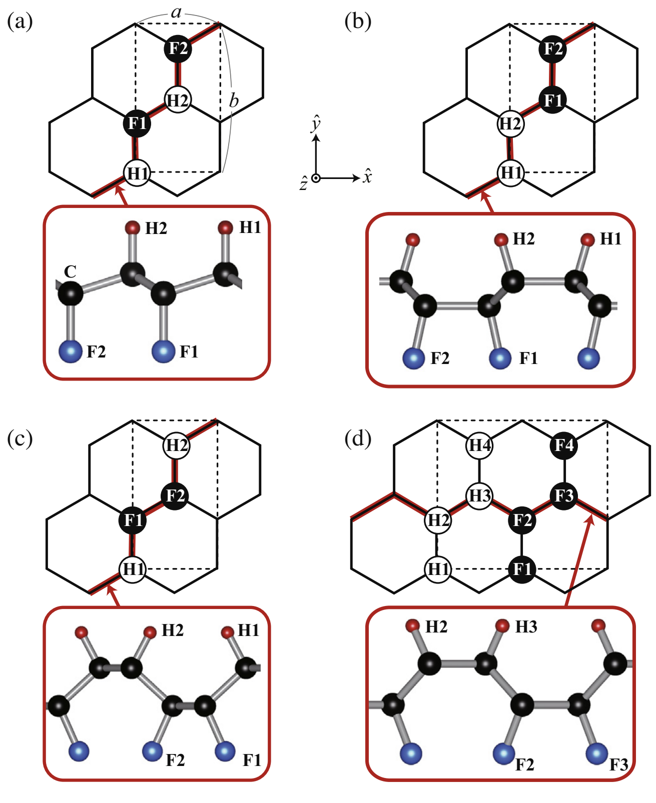

Figure 1. Crystal structures of $(C_2HF)_n$ in (a) chair, (b) boat, (c) zigzag, and (d) armchair conformations. Dashed-line rectangles represent conventional unit cells of $(C_2HF)_n$. Open (solid) circles indicate that hydrogen or fluorine atoms are located on (under) the carbon layer. Side views along the red lines are shown in red boxes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In order to examine the stability of the four different conformations, we calculated the formation energy of each structure. The formation energy of $(C_2HF)_n$, $E_{\mathrm{f},(C_2HF)_n}$, is defined as the difference between the energy of the product $(C_2HF)_n$ and that of the three reactants (graphene, hydrogen gas, and fluorine gas), i.e., $E_{\mathrm{f},C_2HF} = E_{C_2HF} - \left[E_{\mathrm{graphene}} + \frac{1}{2}\left(E_{H_2} + E_{F_2}\right)\right]$. In our calculations, the formation energies of the chair, boat, zigzag, and armchair conformations are −1.883, −1.599, −1.70, and −1.487 eV/C_2HF, respectively. The chair conformation is the most stable one while the armchair conformation is the most unstable. And the zigzag conformation is more stable than the boat conformation. The average distances between two nearest-neighbour F atoms of chair, boat, zigzag, and armchair conformations are 2.58, 2.40, 2.47, and 2.32 Å, respectively. Since F atoms are negatively charged, the Coulomb repulsive interaction between two anions of the chair conformation will be the lowest and that of the armchair conformation will be the highest. Due to this reason, we can expect that the chair conformation will be the most stable conformation while the armchair one the most unstable conformation. The same behaviour can be observed for the boat and zigzag conformations.

The band structures and density of states in Figure 2a–e show that the chair, boat, and zigzag conformations have a direct band gap at the Γ point while the armchair conformation has an indirect band gap. The band gaps of the four conformations are shown in Figure 2f with GGA and GW. Since a lot of empty bands are necessary for the GW calculations, a series of band gaps were obtained from various numbers of empty bands and extrapolated to estimate the fully converged band gap [33]. In our calculations, the armchair conformations have the largest band gap energy (6.7 eV), and the zigzag conformations has the smallest one (5.7 eV). For the chair conformation, we obtained the band gap of 6.0 eV, which was comparable to the previously reported result [34].

3.2. Piezoelectricity of 2D materials

The piezoelectric properties were examined in terms of the piezoelectric stress tensor e_{ij} and the piezoelectric strain tensor d_{ij}, which were defined as [35]

$$e_{ij} = \left.\frac{\partial P_i^d}{\partial S_j}\right|_{\vec{E}}, \qquad d_{ij} = \left.\frac{\partial P_i^d}{\partial \sigma_j}\right|_{\vec{E}}, \tag{1}$$

where P_i^d is the dipolar polarization along the direction i, $\vec{E}$ is the electric field, and S_j and σ_j are the jth component of strain and stress tensors, respectively, in a Voigt notation [36]. We confirmed that the dipolar polarization P_i^d obtained from the Berry phase calculation [37] was similar to that from the electronic charge density and the atomic valence charges. By the Maxwell relationship for the energy per unit volume with respect to external electric field and strain (stress) [35], the tensors can also be written as

$$e_{ij} = -\left.\frac{\partial \sigma_j}{\partial E_i}\right|_{\vec{S}}, \qquad d_{ij} = \left.\frac{\partial S_j}{\partial E_i}\right|_{\vec{\sigma}}. \tag{2}$$

In Eqs. (1) and (2), the piezoelectric tensors describe a linear relationship between a vector (dipolar polarization $\vec{P}^d$ or external electric field $\vec{E}$) and a 6-dimensional vector (stress $\vec{\sigma}$ or strain $\vec{S}$). Stress components in Voigt notation are indicated as $\sigma_1 = \sigma_{xx}$, $\sigma_2 = \sigma_{yy}, \sigma_3 = \sigma_{zz}, \sigma_4 = \sigma_{yz}, \sigma_5 = \sigma_{zx}$, and $\sigma_6 = \sigma_{xy}$ [36]. For the 2D layer structure, the 1 (xx), 2 (yy), and 6 (xy) components are meaningful, and the number of independent components can be reduced due to crystal symmetry. The independent components are $e_{31}(d_{31})$ and e_{22} (d_{22}) for the chair conformation, and e_{31} (d_{31})