Quantitative relation between the structural stability and the aromaticity of graphene nanoflakes

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Recently, nano-scale graphene nanoflakes (GNFs) have attracted great attention as one of the promising materials for electronics and spintronics. Kim et al. have successfully fabricated GNFs with various sizes up to 35 nm and have reported that the photoluminescence property of GNFs depends on the size and the edge shape [1]. From the view point of the structural stability of GNFs, we have not yet acquired the systematic comprehension with regard to effects of shapes and sizes of GNFs on the stability. In the present study, we have examined how the stability of GNFs is dominated by the edge shape and the size of GNFs, using first-principles calculations within the density functional theory.

In order to evaluate the stability of GNFs, we calculated the edge formation energy. First, we consider GNFs with the six-fold symmetry (D_{6h}) and classify them into zigzag GNFs (ZZGNFs) and armchair GNFs (ACGNFs). ACGNFs have two subtypes, AC(1) and AC(2), depending on whether carbon atoms are just at the corner of the outermost envelope hexagon of GNFs. In addition, we also evaluate the structural stabilities of triangular and rhombus GNFs.

Figure 1(a) shows the edge formation energy of the GNFs. The formation energy of ZZGNFs is higher than that of ACGNFs irrespective of the size of GNFs. This instability of ZZGNFs is attributed to the presence of the so-called edge state. Indeed, it has also been shown that the formation energy of the zigzag graphene nanoribbon is higher than that of the armchair one. It is noted that AC(2) is slightly more stable than AC(1), whereas the purity of AC(2) is lower than that of AC(1). Such peculiar stabilization can be reasonably explained in terms of the aromaticity of GNFs. Figure 1(b) shows the rela-tionship between the edge formation energies and the average NICS values. In addition to ACGNFs, we calculated those for trigonal-GNFs and rhombus-GNFs. As clearly seen, the edge formation energy is proportional to the average NICS value. The slope is almost the same for each type of GNFs and the intercept depends on the type. The average NICS values have one-to-one correspondence with the formation energy regardless of the GNF size. This means that the stability of the GNF edge is dominated by the degree of the aromaticity over the whole rings of GNFs. Therefore, it is concluded that the NICS values are not just the measure of aromaticity but also are relevant to the structuralstability of GNFs [2].

[1] S.Kim *et al.*, *ACS Nano*, **6**, 9, 8203 (2012)

[2] A.Akaishi, M.Ushirozako, H.Matsuyama, and J.Nakamura, *Jpn.J.Appl.Phys.* **57** (2018), in press.

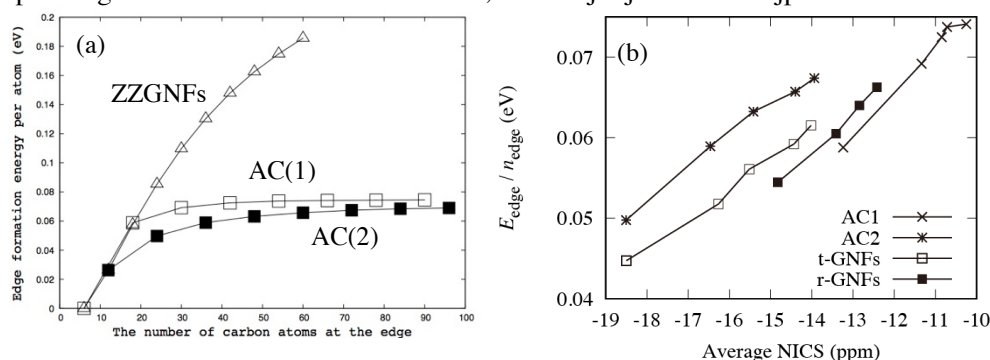* Corresponding author: Prof.Dr. Jun Nakamura, e-mail: junj@ee.uec.ac.jp

Fig. 1 (a) Edge formation energies of GNFs as a function of the number of edge carbon atoms.
(b) Edge formation energy per edge atom versus the average NICS values.

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We have examined the stabilities of GNFs and doped GNFs and related them to the aromaticity by means of NICS values. The stability of non-doped GNFs is dominated by the following factors: (i) The formation of zigzag edges make GNFs unstable because of the existence of the edge states. (ii) The average NICS values have a strong correlation with the structural stability regardless of the shape of GNFs. For both nitrogen-and boron-doped GNFs, the dopant atom is preferably doped near the zigzag edges. This is because the electron/hole from the nitrogen/boron atom migrates to the unoccupied/occupied edge states [S1]. Even for doped GNFs, the average NICS values have positive correlation with the doping formation energy (Fig.S2), whereas the six-membered rings around the dopant become anti-aromatic (Fig.S1).

The so-called Clar formula [S2] is useful to describe the resonance structure of PAHs in terms of the aromaticity. As for doped systems, however, it is not always valid to predict the aromatic rings using the Clar formula, since the number of pi electrons for dopants and neighboring carbon atoms is not necessarily predictable unlike non-doped carbon systems. In spite of the lack of the Clar structure, for the nitrogen- and boron-doped ZZGNF systems, the NICS value is certainly a good measure to predict the structural stability. It has been clarified that the aromaticity is relevant to the stability not only for GNFs but also for doped GNFs, where the Clar formula is necessarily applicable.

[S1] Y.Uchida, S.-I.Gomi, H.Matsuyama, A.Akaishi, and J.Nakamrua, *J.Appl.Phys.* **120**, 214301 (2016).
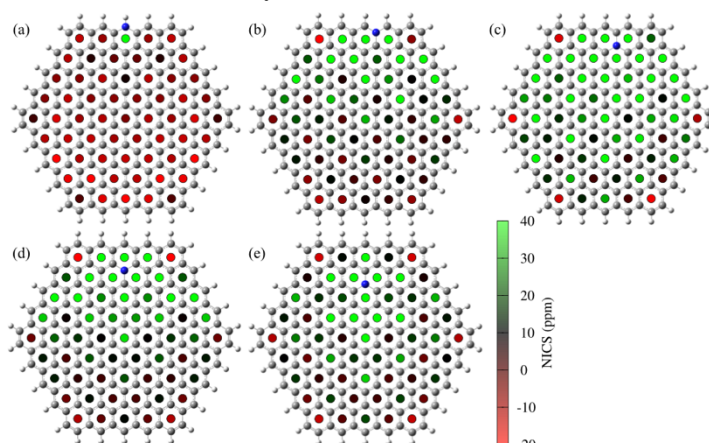[S2] E. Clar, *The Aromatic Sextet*, London, Wiley (1972).

Fig. S1 NICS maps, NICS values for each six-membered ring, for the N-doped GNFs. One nitrogen atom is doped at the edge (a), the second site from the edge (b), thrid (c), fourth (d), and fifth (e). The lower the NICS value, the higher the aromaticity.
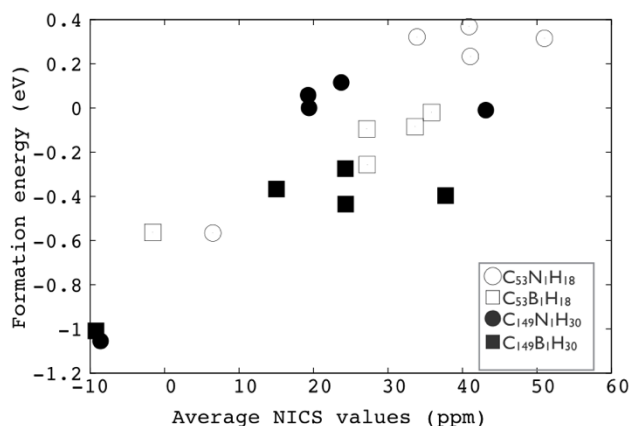

Fig. S2 Edge formation energies vs. average NICS values for the N-Doped GNFs. The edge formation energy and the averaged NICS value are correlated with each other as well as the non-doped GNFs. It should be addressed that the NICS value is a good measure not only for the aromaticity but also for the stability in the pi-conjugated systems even containing nitrogen and boron atoms.