Nanoelectronics based on graphene has become a fast growing field with a number of technical applications. In these circumstances, we perform numerical study of the existence of flat bands (FB) in graphene ribbons, in consideration of zigzag and Klein's bonds with periodic distribution for all cases in which \( N \), \( K \), the density of the Klein's bonds (\( \alpha \)), \( R \equiv N K / 2 N \); These are type (i) where \( \alpha \) decreases, type (ii) ribbons that have only FB, type (iii) ribbons possessing only partially flat band (PFB), and type (iv) containing both FB and PFB. When \( N \) increases in type (iv), double degeneracy of PFB is maintained, while degeneracy of FB increases. Systems of \( N \) = 3n are classified into categories types (i) and (ii), while systems of \( N \) \( \neq \) 3n belong to types (iii) and (iv). We would like to emphasize that above properties for appearances and disappearances of PFB and FB are dominated only by numbers of Klein's bonds in corresponding unit cells for \( N \) periods. Namely, those are independent of positions of Klein's bonds. The relationship between those properties in ribbons and the role of Dirac \( K \)-points originating from graphene is discussed.

Key words: graphene ribbon, edge state, Klein's bonds, Dirac

1. INTRODUCTION

Recently, graphene, i.e. the monolayer of graphite, plays an important role to the extension of material science \([1]-[3] \). In fact, it is stable and has a unique \( \pi \) electronic system. In short, graphene has a hexagonal honeycomb structure of carbon atoms. Many investigations have been made for the characteristic features of graphene \([1]-[11] \). Furthermore, the presences of edge structure of graphene ribbon have been examined over the past decade \([12]-[17] \).

In experiments of graphene ribbons performed in the recent several years, the stability of the zigzag edge, electronic current has been confirmed using advanced technology \([17]-[24] \). However, it has been well-known from viewpoint of experimental investigations that several technical difficulties remain in producing smooth zigzag and armchair edges by conventional physicochemical methods. For example, lithographic etching and chemical methods usually result in rough edges, and some of the edges tend to be broken during preparation and processing \([21] \). The study for material science of graphite has spread from the consideration of infinite sheets without defects to studying the properties of graphene ribbons with imperfections. In particular, noticeable edge effects have been investigated extensively in the past several years \([18], [21]-[24] \).

It should be noted that such an edge state has a large density of states (DOS) at Fermi energy. The graphene ribbon with zigzag edges showed noticeable features in these reports, which were discussed with relation to the property in which the number of sublattices (\( N \)) is equal to the number of B sublattices (\( N_B \)), or \( N_A \neq N_B \). When the system has the condition \( N_A \neq N_B \), the difference of number of sublattice sites produces flat bands. In addition, the presence of flat band produces flat band ferromagnetism, when the system has interaction between electrons \([25] \). Concerning the flat band ferromagnetism of graphene ribbon, it is well known that magnetic moment was made at the edges of the system \([16], [17], [26]-[29] \).

On the other hand, flat band with \( N_A = N_B \) is essentially intrinsic. From now on, we focus on electronic systems under the condition \( N_A = N_B \).

From the viewpoint of edge structure of graphene ribbon, a graphene ribbon with zigzag edges was examined theoretically by Fujita \textit{et al} \([12]-[15] \). In order to analyze the electronic state of graphene ribbon, they use tight-binding model. The zigzag edge is well confined to give rise to partially flat band (PFB) in Brillouin zone (BZ). They showed that the graphene ribbon with zigzag edge had the localization of electron at Fermi energy. By effect of its edge structure, the wavefunction is localized at the zigzag edges. They called the electronic state “edge state”.

In addition, Klein reported a study of systems in which bonds, known as Klein's bonds, were attached to graphene with zigzag edges \([30] \). The graphene ribbon with Klein's bonds also had a PFB at the Fermi energy, and the wavefunction of the PFB is localized at sites surrounding both edges of the ribbons. In ref. \([31] \), the relationship between PFB and the perfectly conducting channel is discussed.

Recently, we examine the relationship between edge structures and electronic states by the use of systems where super lattice structures made by alignments of Klein's bonds on the zigzag edges. In fact, Wakabayashi \textit{et al} use transfer matrix method in ribbons with double periodicity \([32] \). The results are as follows: (\( \alpha \)) PFB appears at Fermi energy in the region of \( 2 \pi / 3d \leq ky \leq \pi / d \), where \( d \) is the distance of a unit cell. (\( \beta \)) The
Dirac K-point exists at $2\pi/3d$ of BZ. (γ) The Dirac K-point is critical point between localization and non-localization of wavefunction. These results of system with double periodicity are treated as the extension of Fujita’s and Klein’s reports [12]-[14].

These previous work gives us the useful perspective regarding electronic properties in ribbons. However, there remains the following problem for systems with periodicities; whether graphene ribbons with $N$ period have always PFB at the Fermi energy, or not. In order to touch the core of the problem, we examine how the electronic state depends on numbers of Klein’s bonds ($N_K$) as well as the periodicity ($N$).

In the present paper, we discuss this problem conducting a survey of all patterns for $2 \leq N_K \leq 2N$ in systems of $3 \leq N$ period. The present paper is organized as follows: We describe the model in Section 2, where a tight-binding model of the energy band is used. In Section 3, the numerical results are shown. Properties of flat bands are discussed in Section 4. In Section 5, the present works are summarized.

2. MODEL

In order to discuss the appearance of a FB (or PFB), we use the density of Klein’s bonds (expressed by $R$) as the ratio between the number of Klein’s bonds ($N_K$) and the number of edges provided by the ribbon with a periodicity ($N$). That is, $R = N_K/N$. We calculate all of the electronic states numerically for $3 \leq N \leq 10$ and $2 \leq N_K \leq 2N$. We use the tight-binding model for the present model,

$$ H = -\sum_{ij} t_{ij} (c_j^+ c_i + c_i^+ c_j), \quad \ldots \ldots \ldots (1) $$

where $c_i^+$ and $c_i$ represent the creation and annihilation operators of electrons at the $i$-th site. With regard to the width of system, there are $m$ rows in the unit cell. The number of rows multiplied by $2N$ gives the number of edge sites in unit cells. In eq. (1), the coefficients $t_{ij}$ are the electron transfer energies between the nearest-neighboring $i$- and $j$-th sites. The FB (PFB) is derived from the eigenvalue $E = 0$ for Hamiltonian eq. (1). In present paper, the FB in systems of $N_A = N_B$ depends both on values of $N$ and $N_K$.

3. NUMERICAL RESULTS

We calculate all cases for graphene ribbons ($N - N_K$ systems) with $3 \leq N \leq 10$ and $2 \leq N_K \leq 2N$ in order to analyze the relationship between various electronic states at $E = 0$ and periodicity ($N$). Typical energy bands are shown in Fig. 2 and 3. In the present paper, number of rows for $m$ (the width of system) is fixed to be 30. From our study, we show the next four topics.

The first topic is the categories of electronic states depending on the periodicity ($N$). The second topic is the relationship between position of Dirac K-point and periodicity ($N$). The third topic is the relationship between numbers of Klein’s bonds and electronic states. The fourth topic is the relationship between positions of Klein’s bonds and electronic states.

In the first place, the categories of electronic states are discussed. The obtained electronic states at $E = 0$ are classified into four categories: (i) possessing no electronic state, (ii) ribbons that have only FB, (iii) ribbons having only PFB, and (iv) containing both FB and PFB. From now on, we show the energy bands for these categories.
Fig. 2. The energy bands of $N_3 - NK_2$ and $NK_4$. For $N_3 - NK_2$, the system has neither FB nor PFB at $E = 0$. On the other hand, $N_3 - NK_4$ system essentially have a FB at $E = 0$.

With regard to the cases of $N = 3n$ ($n$ is integer), we mention examples: The obtained energy band for $N_3 - NK_2$ provides a marked contrast to that of $N_3 - NK_4$ as shown in Fig. 2. The former has no electronic state at $E = 0$, while FB appears in the latter. The system of $N_3 - NK_2$ is categorized as (i) i.e. the type of no electronic state. Instead of FB, antibonding and bonding bands are formed for $E/t > 0$ and $E/t < 0$, respectively.

The bottom of Fig. 2 shows the energy band of $N_3 - NK_4$. It should be noted that an FB was formed at $E = 0$. Thus, we shall call this system as the type (ii) having only FB. The Dirac $K$-point also appears at $k_y = 0$. In the inset at the top of Fig. 2, we fold the BZ of the original graphene with Klein's bonds at the short dashed lines in order to obtain the BZ of $N_3 - NK_2$ system. The Dirac $K$-point of the original graphene ribbon with a zigzag edge moves to the $k_y = 0$ (Γ point) in this case. The result shows that the Dirac $K$-point exists at the Γ point. Meanwhile, $N_3 - NK_6$ shown in the bottom of Fig. 1 is equivalent to the system with $N = 1$ reported by Fujita et al.[12]-[15].

With respect to the condition of $N \neq 3n$, the electronic states of systems $N_4 - NK_4$ and $N_4 - NK_6$ are presented in Fig. 3. The system of $N_4 - NK_4$ has a PFB at $E = 0$ as shown at the top of Fig. 3, while both an FB and a PFB coexist in $N_4 - NK_6$ at the bottom.

The degeneracy of FB and PFB are illustrated in Fig. 4. Here, the horizontal-axis represents the periodicity ($N$), and the vertical-axis denotes the number of Klein's bonds ($NK$) in the unit cell. As described in section 2, we classify the systems into five regions in terms of the density of Klein's bonds ($R = NK/2N$).

Those regions are summarized as follows; The type (i) ($N = 3n$ and $R = 1/3$) represents stripes region. The type (ii) ($N = 3n$ and $R \neq 1/3$) indicates white region. Up to the present, we treat types with $N = 3n$. In contrast, type (iii) ($N \neq 3n$ and $R > 1/2$) means grey region. Type (iv) is divided into two types as type (iv) - (a) and type (iv) - (b). Here, the type (iv) - (a) ($N \neq 3n$ and $R \leq 1/2$) shows black region. In addition to this, we refer the dark grey region (type (iv) - (b)). This type ($N \neq 3n$, $R \leq 1/5$ in $N \geq 7$) has doubly degenerate FB and doubly degenerate PFB. From the viewpoint of density of Klein's bonds, the systems of the dark grey region are treated as the electronic state of graphene ribbon with zigzag edge (Fujita edge with $N = 1$ period). In fact, the system of $N = 1$, which is composed only of Fujita edges, corresponds to those for (PFB, FB) = (2, 4) as $N = 7$, for (2, 4) as $N = 8$ and for (2, 4) as $N = 10$. 

Fig. 3. The top figure shows the energy band of $N_4 - NK_4$. The $N_4 - NK_4$ system has a PFB at $E = 0$. Meanwhile, the $N_4 - NK_6$ system which has both an FB and a PFB at $E = 0$ are shown at the bottom.
In order to explain this topic, we show the folding of BZ of the graphene ribbon with periodicity $N$. The length $d$ of primitive unit cell for $y$-direction becomes $N a_0$ in the system of $N$. Namely, BZ is set to $-\pi/N a_0 \leq ky \leq \pi/N a_0$.

The positions of Dirac $K$-point for $N = 3 (3n)$, $4 (3n - 1)$ and $5 (3n - 1)$ are illustrated in Fig. 4. The thick line means that a line reaches first BZ by the folding, while the thin line indicates that a line reaches $ky = 0$ (Γ point) by the folding. In detail, the systems of $3n - 1$ and $3n - 2$ have $ky = \text{Dirac } K$-point at $2/3$ of BZ, while the system with $3n$ has Dirac $K$-point at $\Gamma$ point. Thus, we need consider the difference of Dirac $K$-point between $N = 3n$ and other systems.

In the third place, the relationship between numbers of Klein's bonds and electronic state at $E = 0$ of graphene ribbons with period $N$. The vertical axis represents the numbers of Klein's bonds ($N K$), while the horizontal axis indicates the periodicity of the graphene ribbon $N$. We use density of Klein's bonds ($R = N K/2 N$). The line of $R = 1$ indicates that systems have a PFB with $N = 1$, and the solid line represents $R = 1/2$. Here, systems on the dotted line ($R = 1/3$) have no electronic state at $E = 0$. We shall call the system as the type (i). The systems with $N = 3n$ and $R \neq 1/3$ named type (ii) have FB. Regarding cases with $N \neq 3n$ period, the line $R = 1/2$ represents the boundary between systems with only PFB (grey region named type (iii)) and those including both FB and PFB (black region named type (iv) - (a)). In addition to this, the systems in dark grey region called type (iv) - (b) have PFB and FB. We distinguish the system of dark grey region from one of grey region, although the system of type (iv) - (a) and the system of type (iv) - (b) have PFB and FB. The electronic state of dark grey region is treated as Fujita type. Concerning the electronic state of grey region, the system is treated as Klein type.

In the second place, the relationship between Dirac $K$-point and periodicity ($N$) is obtained. In order to explain this topic, we show the folding of BZ of the graphene ribbon with $N = 3n$ periods and $N \neq 3n$ periods. The position of $\Gamma$-point between $N K$-point and periodicity ($N$) in the next section.
In the fourth place, we obtain the relationship between position of Klein's bonds and electronic state. The result shows that the electronic state is independent of the position of Dirac $K$-point. It is a highly non-trivial property. The remarkable property leads us the suggestion of the essential linkage between left and right edges by the aid of effect for Dirac $K$-point originating from graphene ribbon. In relation with electronic properties, the discussion is made in the next section.

4. DISCUSSION

On the basis of numerical results, we examine the relationship between numbers of PFB (or FB) and periodicity ($N$).

In order to analyze the result shown in Fig. 4, we explain the folding of BZ which shifts the position of Dirac $K$-point. In addition, the dependence of electronic state on positions of Klein's bonds is examined.

4.1. The degeneracy of PFB (or FB) and the periodicity ($N$).

The relationship between numbers of PFB and FB alters in consideration of systems with double and quadruple periods, even if the equivalent configuration is treated. An example is shown here. The energy bands of $N2 - NK2$, $N4 - NK4$ and $N8 - NK8$ systems are shown in Fig. 6. We explain the degeneracy of FB (or PFB) and in relation with the shift of the position for Dirac $K$-point.

The system of $N2 - NK2$ possessing PFB has the Dirac $K$-point at $k_y = \pi/3a_0$. When $N2 - NK2$ system is folded at the line of $k_y = \pi/4a_0$, the energy band of $N4 - NK4$ system is made as illustrated in Fig. 6 - (b).

The $N4 - NK4$ has only PFB (double degeneracy). As the result of refolding at the line of $k_y = \pi/8a_0$, the $N8 - NK8$ system is constructed as shown in Fig. 6 - (c). This system has double FB and PFB at $E = 0$. In summary, the degeneracy of PFB keeps to 2 by the present folding procedure, while that of FB changes.

4.2. The dependence of electronic states on positions of Klein’s bonds

In this subsection, the relationship between electronic states and numbers of Klein’s bonds for each system with periodicity ($N$) is discussed.

Fig. 7. The illustrations indicate the configurations of the system of $N4 - NK4$. Here, the configuration (E) is as same as system of Fig. 6 (b).

Fig. 8. The charge densities labeled the configuration (S) for $N4 - NK4$ system. Top and bottom of figures show charge density of the configuration (S) shown in Fig. 7 with $k_y = 0$ and $k_y = \pi/6a_0$. Under the
symmetric configuration of Klein's bonds, the charge density is symmetric structure. In the inset, the equivalent network for tight-binding model of the graphene ribbon is given.

Fig.9. The charge densities labeled the configuration (D) for $N4 - NK4$ system. The configuration (D) has non-symmetric structure. Top and bottom of figures indicate charge densities of the configuration (D) shown in Fig. 7 with $ky = 0$ and $ky = \pi/6a_0$. In the inset, the equivalent network for tight-binding model of the graphene ribbon is given.

It is noticeable result obtained in this work that numbers of PFB and FB for $N - NK$ systems are independent of positions of Klein's bonds. For example, we discuss the problem of the positions of Klein's bonds by using the configurations of $N4 - NK4$ system shown in Fig. 7. These configurations have same the degeneracy of PFB and FB, though six patterns can be constructed as shown in Fig. 7.

In order to explain this fact, we use the configuration (S) and the configuration (D). The configuration (S) has symmetric configuration of Klein's bonds, while the configuration (D) has non-symmetric configuration of Klein's bonds. Namely, it is in default with symmetry as shown in Fig. 7. Concerning to the difference of the configuration of Klein's bonds, we analyze the charge densities of these configurations (S) and (D).

Here, the equivalent network for tight-binding model of the graphene ribbon is given in the inset of Fig. 8 and 9. On the basis of the descriptions of the insets, the charge densities of configurations (S) and (D) are shown in Fig. 8 and 9. These figures indicate those charge densities for $N4 - NK4$ system for $ky = 0$ and Dirac $K$-point. The configuration (S) has the symmetric charge density as shown in Fig. 8, while the configuration (D) has the non-symmetric charge density as shown in Fig. 9.

We adopt the plane whose axes are numbers of rows ($m$) and sites numbers ($l$) in Fig. 8 and Fig. 9.

When the $ky = 0$, both configurations (S) and (D) have finite densities around Klein's bonds. In addition, charge densities of configurations (S) and (D) disappear around inner sites. Namely, it is made clear that the electron localizes at the Klein's bonds of the configurations (S) and (D) for $ky = 0$.

On the other hand, charge densities have a finite value both around Klein's bonds and inner sites in the configuration (S) and (D) at the $ky = \pi/6a_0$ (Dirac $K$-point). In particular, the amplitude at Klein's bonds is six times as large as that of inner sites. From these results, it should be noted that the flatness of energy band is kept from $ky = 0$ to $ky = \pi/6a_0$ (Dirac $K$-point) in spite of changing the position of Klein's bonds. Here, charge density quickly damps for inner sites. When $ky$ is deviated from Dirac $K$-point. Thus, the edge structure causes strong charge localization close to the edge even near the Dirac $K$-point. Our results are the natural extension from Fujita's and Wakabayashi's reports for systems of $N = 1$ and 2 [12]-[15], [32]. However, we have no discussion on changes of the position of Klein's bonds, because they didn't treat the graphene ribbons with $3 \leq N$.

Moreover, the difference of charge densities between configurations (S) and (D) is obtained. The difference of charge density is found only around sites of Klein's bonds. In contrast, we cannot distinguish the difference of charge densities in inner sites. This fact leads us the suggestion that the non-local properties in the inner sites are quite persistent because of the essential effect of Dirac $K$-point.

5. CONCLUSION

In the present work, we discuss the electronic states at $E = 0$ of graphene ribbons in regard to FB and PFB with various Klein's bonds, which depend on the periodicity $N (3 \leq N \leq 10)$ and the number of Klein's bonds $NK$ ($2 \leq NK \leq 2N$). We would like to emphasize that non-local properties of Dirac $K$-point are quite obstructive even for systems with multiple periodicity by edge modification.

The electronic state at $E = 0$ are categorized into four types: (i) possessing no electronic state at $E = 0$, (ii) ribbons that have only FB, (iii) ribbons having only PFB, and (iv) contains both FB and PFB.

Moreover, our study makes clear the fact that the appearance of FB and PFB are independent of the positions of the Klein's bonds. These are noticeable phenomena, although there remain unsolved problems in obtaining analytical solutions.

The results are considered as the extension from obtained properties of graphene ribbons with $N = 1$ and 2 periods. As a new prediction, we insist that the systems with $N = 3n$ and $R = 1/3$ are quite unique in comparison with Fujita's report and Wakabayashi's work; Dirac $K$-point exists at the $ky = 0$ (Γ point). We find that the wavefunction of this case cannot satisfy with the equation for the eigenvalue $E = 0$ for Hamiltonian eq. (1) at $ky = 0$ from numerical calculation. In other word, the electronic states at $E = 0$ does not exist. As a result of splitting of bonding and
anti-bonding level, the system for the \( N = 3n \) and \( R = 1/3 \) has no electronic state at \( E = 0 \). This prediction cannot be derived from calculations with \( N = 2 \) [32].

In the discussion of folding of BZ, the position of Dirac \( K \)-point is determined. However, the electronic states cannot be explained only by the position of Dirac \( K \)-point.

For cases of \( N = 3n \), we are faced with the problem why the electronic state of \( N3 - NK2 \) is different from that of \( N3 - NK4 \), although both systems have Dirac \( K \)-point at \( ky = 0 \) under the condition of \( N = 3 \) periodicity. Namely, we need consider the position of Dirac \( K \)-point and the numbers of Klein's bonds.

In regard to ribbons with \( N \neq 3n \), Dirac \( K \)-points appear at 2/3 of BZ by folding for formation of periodicity (N). In categories type (iii) and (iv), the degeneracy for states at \( E = 0 \) is maintained in the region from \( ky = 0 \) to \( 2 \pi/3d \) or that from \( 2 \pi/3d \) to \( \pi/d \). Further, type (iv) contains several additional FB. To sum up, it is certain that numbers of PFB and FB are determined by the numbers of Klein's bonds. However, it must be noted that those degeneracy of PFB and FB don't rely on positions of Klein's bonds.

Future studies will focus on the problem of the effect of interactions with long ranges, e.g., next-nearest neighbor hopping, to electronic states of FB or PFB from viewpoint of material science. This problem is the topic of our further study. We hope that our work will give clue to future experimental investigation of graphene ribbons with various kinds of edge modifications.

Acknowledgement

The authors thank Professor T. Hanawa of Chiba University and Dr. K. Wakabayashi (WPI-MANA, NIMS) for helpful discussions.

References


(Received June 8, 2010; Accepted July 10, 2010)