I. INTRODUCTION

In the previous reports \[20, 21\], the temperature-dependence of the electric conductivity (TDEC) of activated carbon fibers (ACFs) was investigated, which are known as highly disordered systems (HDSs) \[8\]. A mechanism of activational hopping conductivity for the disordered systems was proposed that thermal excitations with the Wigner surmise,

\[
p_{WS}(E_G)dE_G = 2(E_G/R_0^2) \exp(-E_G^2/R_0^2) dE_G, \quad (I.1)
\]

contribute to the conductivity. The mechanism provides the TDEC which is in good agreement with the experimental results of Kuriyama \[14\] and reproduces the (apparent) metal-insulator transition in \[15\].

Further in \[20, 21\], it was microscopically assumed that the Wigner surmise comes from the quantum chaos in the small particles because the ACFs consists of small pieces of graphite \[8\]: each piece of small graphite might be regarded as a quantum box and it is known that its energy eigenvalue is described well by the random matrix theory (RMT) and obeys the Wigner surmise \[11, 22\].

In this article, we revise the assumption and employ another origin of the Wigner surmise based on the recent investigation of graph zeta function in graph theory.

II. RESULTS OF THE PREVIOUS REPORT

Here we will review the formula in \[20, 21\] on the TDEC in HDCs or the ACFs with the temperature \(T_{HT}\) of the HTP as a parameter.

As mentioned in \$I\$, by employing the Wigner surmise \[11\] as the DOS, the total conductivity is expressed by

\[
\sigma_{total}(T) = \sigma_0(T) \int dE_G p_{WS}(E_G) \exp(-E_G/k_B T)
\]

\[
= \sigma_0(T) \left[ 1 - \sqrt{\frac{\alpha}{T}} \exp\left(\frac{\alpha^2}{T^2}\right) \cdot \text{erfc}\left(\frac{\alpha}{2T}\right) \right],
\quad (II.1)
\]

where \(\alpha\) is a fitting parameter depending on \(T_{HT}\), and \(\sigma_0(T)\) weakly depends on the temperature \(T\), \(\sigma_0(T) = \sigma_0^{(0)}(1 + \delta T)\). Then \(II.1\) reproduces well the experimen-
tal results \[14\] including the insulator-metal transition \[15\] as in FIG. 1.

FIG. 1. TDEC: The dotted points show the experimental results of TDEC $\sigma_{\text{total}}(T)/\sigma_{\text{total}}(250[K])$ for as-prepared (AS) and heat-treated ACFs and curves following \(11, 13\) for fitting parameters $a$ and $a^{-1} = 1.5 \times 10^{5}[K^{-1}]$.

As mentioned in §I, it was considered in \[20, 21\] that the origin of the Wigner surmise \(11\) was quantum chaos for the quantum boxes since the graphite pieces of the ACF might be regarded as small granular particles. For example, the quantum system of stadium is governed by the RMT. The Wigner surmise naturally appears in the RMT since each level is repulsive in \[1, 22\].

III. ELECTRIC STRUCTURE OF GRAPHITE

The electronic property of graphite has been studied well. The tight-binding approximation (TBA) of $\pi$-electron distribution of graphite as a 2D honeycomb lattice was studied in \[3, 27\]. Coulson and Taylor also considered effects of overlap integrals and 3D effect \[3\]. Zunger investigated a more realistic model \[28\].

In these studies, the infinite size of lattice or pure crystal of graphite was assumed. On the other hand, as in \[8, p.71\] and \[8\], the ACFs consists of small pieces of graphite and the HTP of the ACFs modifies the structure and the size of the pieces drastically.

The boundary of the graphite piece is not stable due to dangling bonds. Since the phonon is easily excited there, the coherency of the electron wave function is loosed there. Since the ACF is considered as a collection of small graphite pieces, the electronic band structure is given as that of independent pieces as in \[8, p.153-161\].

In the picture, since the shape of the piece is crucial, we go back to the TBA as a simple approximation \[23\].

IV. THE TBA AND THEORY OF GRAPH

We consider the electronic structure of the small graphite pieces in the framework of the TBA. For a given graph $\mathcal{G}$, e.g. FIG. 4 let the set of nodes in $\mathcal{G}$ denoted by $\mathcal{N}_G$ and that of edges in $\mathcal{G}$ by $\mathcal{E}_G$. For the real numbers $\varepsilon_0$ and $\gamma_0 = 3.16[eV] \ [8, p.160]$, the hamiltonian of $\mathcal{G}$ is given by $H = \varepsilon_0 D_G - \gamma_0 A_G$, where $D_G$ is the diagonal matrix and $A_G$ is the adjacency matrix of the graph $\mathcal{G}$; for every $i, j \in \mathcal{N}_G$, $(D_G)_{ij} = \delta_{ij}$, and $(A_G)_{ij} = 1$ if there is an edge $(i, j)$ in $\mathcal{E}_G$ otherwise vanishes \[2, 7\]. $H$, $D_G$, and $A_G$ are $N \times N$-matrices for $N = |\mathcal{N}_G|$. The spectrum of $H$ is determined by the SAM $A_G$ \[2\].

In the graph theory, Ihara’s zeta function and the SAM have been studied as a graph theoretic version of the Riemann hypothesis \[13, 25\]. As in \[22\], since many observations show that mathematical properties of the Riemann zeta function associated with Riemann hypothesis are expressed well by the RMT, the graph zeta function and SAM should be also described by the RMT. It is shown that for a certain (random) graph, the Wigner semicircle law governs the SAM \[24, 25\].

Further Newland, in his thesis 2005, showed by numerical computations that in a certain graph, the spectra of the adjacency matrices and Ihara’s zeta functions obey the Wigner surmise \(11\) \[25, p.41\].

The SAM of the infinite 2D graphite lattice or the honeycomb lattice was obtained by Coulson and Rushbrooke \[3\] and, later, was precisely studied by Horiguchi in terms of the lattice Green function method \[3, 10\]. The DOS is explicitly written by

$$
\rho_{\text{HC}}(\mu) = \begin{cases} 
\frac{2\sqrt{3\pi}}{3\sqrt{3\mu^2}} \mathcal{K}(\kappa(\mu)) & \text{for } 1 < |\mu| < 3 \\
\frac{2\sqrt{3\pi}}{3\sqrt{3\mu^2}} \mathcal{K}\left(\frac{1}{\pi|\mu|}\right) & \text{for } |\mu| \geq 1
\end{cases}
\tag{IV.1}
$$

where $\mathcal{K}$ is the Jacobi elliptic integral of the first kind and

$$
\kappa(\mu) = \frac{1}{\mu} \sqrt{1 + \frac{1}{|\mu|}} \frac{1}{\mu}
$$

as in FIG. 2. It is also noted that Ihara’s zeta function of the infinite lattice is related to the elliptic integral \[4\].

FIG. 2. The DOS of the 2D Honeycomb lattice

The SAM of a small piece of graphite asymptotically approaches to the DOS \(\rho_{\text{HC}}\) when its size approaches to $\infty$. It is contrast to the fact that for a certain class of the random graph, the asymptotic behavior of the DOS obeys the semicircle law \[24\].

However it is expected that the density of the level-spacing of the SAM is determined by a function similar to the Wigner surmise \(11\) because 1) the degenerate states are naturally avoided if there is no global symmetry and 2) the average of the level spacings must be determined by the insertions of $|\mathcal{N}_G|$ points into the region $[-3, 3]$. 

V. CONDUCTIVITY OF THE ACFS

Let us employ the ansatz that the level statistics of the graphite piece obeys the Wigner surmise (I.1). Though the gap of the first excited state from the Fermi level (the gap between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital)) is concerned only, it is natural to assume that the gap also obeys the Wigner surmise (I.1) from recent development of the graph theory mentioned above [25].

In the framework of the TBA, the occupied states depend on the number of the carbon atoms and due to the spin effect; there is the gap if the number is even whereas the state is not filled if the number is odd. Though depending on the parity of each graphite piece, there appears the following picture as a large resistance case.

![Hopping process from (a) to (b).](image)

FIG. 3. Hopping process from (a) to (b).

Let us consider the hopping phenomena between two adjacency graphite pieces. As in illustrated in FIG. 3 in order that an electron in a piece hops to its adjacency one, the electron must jump to excited states as the first step. Under the electric field, the possibility of hopping is influenced and we have finite conductivity.

Let us consider that the ACF is arranged between two electrodes. From one electrode to another, there are possible electric paths \( C_a : \{C_a\} \). Let \( \sigma_{i,j} \) be the local conductivity of adjacency graphite pieces belonging to the path \( C_a \). The conductivity \( \sigma_{C_a} \) along the path \( C_a \) could be approximated by

\[
\sigma_{C_a} = \left( \sum_i \frac{1}{\sigma_{i,i+1}} \right)^{-1} \approx \left( \max_i \frac{1}{\sigma_{i,i+1}} \right)^{-1}.
\]

Then the total conductivity is simply obtained by the summation over all paths, \( \sigma_{\text{total}} = \sum_{C_a \in \Gamma} \sigma_{C_a} \). It means (III.1) and the above picture shows its microscopic origin.

VI. NUMERICAL STUDY

We, first, numerically showed the justification of the ansatz in §V for graphs given as FIG. 4 using the software Graphtea; we computed their SAM \( \{\mu\} \) by solving \( \det(\mu I - A_G) = 0 \) numerically. Let the distribution of the SAM denoted by \( \rho_G \) and that of level spacings by \( p_G \). The results are illustrated in FIG. 5 which shows that \( \rho_G \) approach to \( \rho_{WS} \) asymptotically and \( p_G \) is similar to \( p_{WS} \) due to the level repulsion. In other words, our ansatz in §V is natural. In fact, FIG. 5 exhibits that \( p_G \)'s are approximated by the Wigner surmise (I.1).

![Numerical Results of \( \rho_G \) and \( p_G \).](image)

FIG. 5. Numerical Results of \( \rho_G \) and \( p_G \).

We computed the center of the gravity for \( p_G \)'s, i.e., \( \int \mu p_G(\mu)d\mu \), and the effective \( \alpha \) for \( \gamma_0 = 3.16[\text{eV}] \) noting \( \int_0^{\infty} p_{WS}(\mu)\mu d\mu = \frac{\sqrt{\pi}}{2}\gamma_0 \) as in Table 1:

Using the least mean square method, the relation between \( \alpha \) and the number \( N = |N_G| \) is evaluated as \( \alpha = 2.8 \times 10^5/[N][K] \) from Table 1. With the estimation \( N = \pi(R/a)^2 \) for the radius \( R \) and \( a = 0.142[\text{nm}] \),
the fitting parameters \( \alpha \)'s in FIG. 1 are reduced to the effective radii \( R \)'s as in Table 2.

| case | \( \alpha \) [K] | N | \( R \) [nm] |
|------|--------------|---|---------|
| I    | 180          | 1.6 \times 10^3 | 3.2   |
| II   | \( T_{HT} = 860[^{\circ}\text{C}] \) | 40.7 \times 10^3 | 6.7   |
| III  | \( T_{HT} = 1000[^{\circ}\text{C}] \) | 20 \times 1.4 \times 10^4 | 9.5   |
| IV   | \( T_{HT} = 1200[^{\circ}\text{C}] \) | 0.1 \times 2.8 \times 10^3 | 1.3 \times 10^2 |

Since X-ray analysis shows that there is a 1.1[nm] peak which corresponds to the length along c-axis of three stratified graphite sheets \([8, 9]\). Thus by considering 3D effect, \( R \)'s of case I-III in Table 2 should be divided by several numbers. From p.71 in \([8]\), the structure of the ACF strongly depends on \( T_{HT} \) of HTP and especially around \( T_{HT} = 1500[^{\circ}\text{C}] \), the structure drastically changes and has 3D property as a kind of structural phase transition. However the critical temperature \( T_{HTC} \) also depends on the material origin of the ACFs. Thus the ACF of case IV may have the 3D structure and if we use \( N = 4\pi R^2/3\alpha^3 \), \( R = 12[^{\circ}\text{mm}] \). Then these estimations of \( R \)'s are compatible with TEM data in \([8]\) and it also turns out that the (apparent) metal-insulator transition might come from the structural transition due to the HTP.

| case | \( \alpha \) [K] | N | \( R \) [nm] |
|------|--------------|---|---------|
| I    | 180          | 1.6 \times 10^3 | 3.2   |
| II   | \( T_{HT} = 860[^{\circ}\text{C}] \) | 40.7 \times 10^3 | 6.7   |
| III  | \( T_{HT} = 1000[^{\circ}\text{C}] \) | 20 \times 1.4 \times 10^4 | 9.5   |
| IV   | \( T_{HT} = 1200[^{\circ}\text{C}] \) | 0.1 \times 2.8 \times 10^3 | 1.3 \times 10^2 |

VII. DISCUSSIONS

In this article, we show that the SAM reproduces the conductivity of the disordered carbon system. We conclude that our picture is natural to the TDEC of the ACFs. In the series of works \([11, 18, 19, 22]\), One of the authors (S.M.) has been showing that some of physical phenomena are expressed well by pure mathematical results. Since the SAM appears in theory of the graph zeta function which has been studied as a graph theoretic version of the Riemann hypothesis \([13, 24, 26]\), the TDC of the ACFs is one of such cases.

However the studies on the Wigner surmise of SAM are not sufficient. Especially the gap between HOMO and LUMO of pieces of graphite should be studied more systematically \([17]\). Further since there are studies of more realistic computation of electronic structure of graphite pieces \([2, 3]\), it is expected that the statistical property of gaps for these systems is evaluated in future.

Since recently it is found that Ihara's zeta functions naturally appears in quantum walks \([12]\), it means that this investigation might show another possibility of quantum walk.

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