Pragmatic Application of Abstract Algebra to Two-Dimensional Lattice Matching

Kazuuki Kawahara
Department of Advanced Materials Science, Graduate School of Frontier Science,
The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan, and
Research Fellow of Japan Society for the Promotion of Science,
5-3-1 Koujimachi, Chiyoda-ku, Tokyo 102-0083, Japan

Ryuichi Arafune
International Center for Materials Nanoarchitectonics (WPI-MANA),
National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Maki Kawai and Noriaki Takagi*
Department of Advanced Materials Science, Graduate School of Frontier Science,
The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan
(Received 20 April 2015; Accepted 5 June 2015; Published 11 July 2015)

We investigated the lattice matching condition of two-dimensional (2D) lattices based on the group isomorphism of 2D Euclidean space to complex plane. This isomorphism enables us to avoid the inconvenience derived from the algebraic structure of 2D vectors and provides the systematic analysis. We found that the lattice matching is closely connected with ideal class group which is an invariant in the algebraic number field. We also provide an algorithm to construct a structure model for a superstructure formed by overlapping two 2D lattices, which is helpful for making trial models in the structure analysis. [DOI: 10.1380/ejssnt.2015.361]

Keywords: Surface structure, morphology, roughness, and topography; Structure analysis; Lattice matching; Abstract algebra

I. INTRODUCTION

Fueled by the exotic properties of two-dimensional (2D) materials such as graphene [1-3], transition metal dichalcogenides [4,5] and etc., exploring of one-atom-thick layer materials grown on solid substrates has gathered lots of attention. Challenges have been made to synthesize these novel materials on solid substrates, to reveal their geometric and electronic structures as well as to bring out the hidden properties by lattice engineering and tailoring of the interfacial couplings [6-14]. In these challenges, structure determination is central, which provides solid foundation to figure out their properties and develop device applications. The following basic questions arise about the structure: “Is a 2D overlayer commensurate to a substrate?” and “What type of superstructure is formed by matching the overlayer and substrate?” To answer these questions, we usually describe both overlayer and substrate with 2D vectors and then we search for the conditions of lattice matching in Euclidian 2D vector space. Although this procedure has been widely used, it sometimes annoys us due to the algebraic structure of 2D vector space. The universal set of 2D vectors is neither ring nor field so that we cannot operate two binary operations, i.e., multiplication and division [15]. For instance, it is not easy to answer the problem whether it is possible to stack a 2D lattice commensurately on a 2D lattice. In addition, it is sticky to construct structural model for superstructure with long periodicity which often emerges for graphene grown on transition metal substrates [6-10]. Indeed, we can construct structural models based on the 2D vectors, but we often have concerns if the modeling covers all the reasonable models and rules out the unreasonable ones. These problems come from the formularization based on the 2D vectors.

The group isomorphism of 2D Euclidean space to complex plane enables us to describe a 2D vector as a complex number. Here R is a field of real numbers and C is a field of complex numbers. Since the complex plane is a field where we can perform the four basic arithmetic operations [15], one can avoid the inconvenience and pave the way to consider the lattice matching systematically. In this paper, we build up a theory on lattice matching based on the group isomorphism and provide an algorithm to construct a structural model and design artificial lattice. Hereafter, we use the following symbols: Z, ring of integers, Q, field of rational numbers, and H upper half plane, \( \mathbb{H} = \{ z | z \in \mathbb{C}, \ \text{Im}(z) > 0 \} \).

II. THEORY ON LATTICE MATCHING

First, we define a lattice group which plays a central role in our theory; the lattice group is defined to be a subgroup of \( \mathbb{C} \) consisting of lattice points described as \( \{ \gamma(a + br) | a, b \in \mathbb{Z} \} \). Here, \( \gamma \) is a complex number to specify the size of the unit cell and the rotation angle relative to the real axis, and \( \tau \) is also a complex number in \( \mathbb{H} \) and is an invariant to determine the symmetry of the lattice. Five Bravais lattices in 2D space [16] can be described by setting appropriately as summarized in Fig. 1. For instance, \( \tau = \sqrt{-1} \) and \( \tau = (1 + \sqrt{-3})/2 \) generate square and hexagonal lattices, respectively. These lattice groups correspond to the rings of Gaussian (\( \tau = \sqrt{-1} \))

* Corresponding author: n-takagi@k.u-tokyo.ac.jp
and Eisenstein \((\tau = (1 + \sqrt{-3})/2)\) integers, respectively [15].

Consider a superstructure \((\gamma \Gamma^S)\) formed by stacking a 2D overlayer \((\rho \Gamma^O)\) on a substrate \((\lambda \Gamma^{S\text{Sub}})\). When the superstructure is commensurate to the substrate, \(\gamma \Gamma^S\) is an intersection of \(\rho \Gamma^O\) and \(\lambda \Gamma^{S\text{Sub}}\) so that \(\lambda \Gamma^{S\text{Sub}} \cap \rho \Gamma^O = \gamma \Gamma^S\) holds. Although the superstructure is not always commensurate to the substrate, it is commensurate to the overlayer. Here, we assume that the symmetries of substrate and overlayer are preserved. Thus, the following equation always holds for \(\gamma \Gamma^S\) and \(\rho \Gamma^O\):

\[
\Gamma^S \cap k^{-1} \Gamma^O = \Gamma^S, \tag{1}
\]

here we introduce \(k = \gamma / \rho\) for convenience. We call the equation (1) “structure equation”. The structure equation systematically enables us (i) to judge whether two lattices are commensurate each other and (ii) to construct a model of the superstructure.

Here we discuss the existence condition of solution for the structure equation (1). The condition determines whether a lattice matches commensurately to other lattices. When the structure equation (1) holds, \(\tau\), one of the elements of \(\Gamma^S\), must be an element of \(k^{-1} \Gamma^O\) and then \(\tau = k^{-1}(a\sigma + b)\) where \(a, b \in \mathbb{Z}\). In addition, since the same is true for identity element of \(\Gamma^S\), there exist integers \(c\) and \(d\) which satisfy \(1 = k^{-1}(c\sigma + d)\). These equations give the existence condition of solution that there exist four integers \((a, b, c, d)\) to satisfy \(\tau = \frac{a\sigma + b}{c\sigma + d}\), where \(ad - bc \neq 0\). The condition of \(ad - bc \neq 0\) ensures that the unit vectors of the superstructure are linearly independent.

To demonstrate usability of the structure equation, we take a simple problem as an example. We can answer a following problem by very simple discussion: “Is it possible to stack hexagonal lattice commensurately on square lattice?” When we assume that the hexagonal lattice stacks commensurately on square lattice, \(\tau \in \mathbb{H}\) and eight integers \((a, b, c, d, a', b', c'\) and \(d')\) exist such that \(\tau = \frac{a\omega + b}{c\omega + d} \in \mathbb{Q}(\sqrt{-3})\) and \(\tau = \frac{a'\omega + b'}{c'\omega + d'} \in \mathbb{Q}(\sqrt{-3})\).

from the existence condition. Here \(\mathbb{Q}(\sqrt{-m})\) is imaginary quadratic field and \(\omega = \frac{1 + \sqrt{-3}}{2}\). These two equations give \(\tau \in \mathbb{Q}(\sqrt{-1}) \cap \mathbb{Q}(\sqrt{-3})\) which leads to \(\tau \in \mathbb{Q}\). This is contradicted with \(\tau \in \mathbb{H}\). Therefore, we answer the problem and obtain a proposition that it is impossible to stack hexagonal lattice commensurately on square lattice. In the same manner, a similar proposition, “it is impossible to stack hexagonal lattice commensurately on rectangular lattice”, is also proved. In this proof, we describe the rectangular lattice as \(\Gamma_{\sqrt{2}}\), which is a subgroup of \(\mathbb{Q}(\sqrt{2})\).

The structure equation provides a following theorem on the symmetry relation among overlayer, substrate and superstructure:

**Theorem:** Let \(\Gamma_{\tau}\) be the ring of integers of \(\mathbb{Q}(\sqrt{-m})\) which ideal class group of \(\mathbb{Q}(\sqrt{-m})\) is trivial. If the overlayer \((\rho \Gamma^O)\) is commensurate with the substrate \((\lambda \Gamma^{S\text{Sub}})\), i.e. \(\chi \in \mathbb{C} \setminus \{0\}\) and \(\xi \in \mathbb{H}\) exist such that \(\rho \Gamma^O \cap \lambda \Gamma^{S\text{Sub}} = \chi \Gamma^O \cap \xi \Gamma^{S\text{Sub}}\), then, \(\xi = \tau\).

Among the five 2D Bravais lattices, square and hexagonal lattices are described as \(\Gamma_{\sqrt{2}}\) and \(\Gamma_{\sqrt{3}}\), and thus satisfy the prerequisite. It is intuitively natural that a superstructure formed by two square (hexagonal) lattices is square (hexagonal). This intuition is guaranteed by this theorem. In contrast, oblique, rhombic and rectangular lattices do not always meet the prerequisite so that a superstructure formed by stacking these lattices commensurately is not always in the same symmetry. Figure 2 demonstrates an example. When we put a rectangular lattice \(\Gamma_{\sqrt{2}}\) on another rectangular lattice \(\Gamma_{\sqrt{3}}\), the superstructure is an oblique lattice that is described as \(2\Gamma_{\sqrt{2} + \sqrt{3}}\).

Now let us discuss the algebraic structure behind this theorem. As we consider the case in which the overlayer \((\rho \Gamma^O)\) is commensurate to the substrate \((\lambda \Gamma^{S\text{Sub}})\),
FIG. 3. Honeycomb and hexagonal lattices on the complex plane. Green, orange and red cells indicate the unit cell of superstructure, honeycomb lattice and hexagonal lattice, respectively.

\[ \lambda \Gamma_{\text{Sub}} \cap \rho \Gamma_{\sigma}^O = \chi \Gamma_{\xi}^{S} \] holds. This equation leads to the following structural equations: \( \Lambda \Gamma_{\tau}^{S} \cap \chi \Gamma_{\xi}^{S} = \chi \Gamma_{\xi}^{S} \) and \( \rho \Gamma_{\sigma}^O \cap \chi \Gamma_{\xi}^{S} = \chi \Gamma_{\xi}^{S} \). These equations indicate that there exist two complex numbers \( k_0 \) and \( k \) which satisfy \( k_0 \lambda = k \rho = \chi(k_0, k) \in \Gamma_{\tau} \). Thus, \( \lambda \Gamma_{\text{Sub}} \cap \rho \Gamma_{\sigma}^O = \lambda \Gamma_{\text{Sub}} \cap \frac{\rho}{\lambda} \Gamma_{\xi}^{S} = k_0 \lambda \Gamma_{\xi}^{S} \). Here we can set \( \lambda = k \), because \( \lambda \) is a non-zero arbitrary complex number and determine the sizes and angles of overlayer and superstructure lattices. Then, \( k \Gamma_{\text{Sub}} \cap k_0 \Gamma_{\xi}^{C} = k k_0 \Gamma_{\xi}^{S} \). Since \( \Gamma_{\tau} \) is a ring, both \( k \Gamma_{\text{Sub}}^{S} \) and \( k_0 \Gamma_{\xi}^{C} \) are principal ideals of \( \Gamma_{\xi} \) and are written as \( (k) \) and \( (k_0) \) following the mathematics notation, respectively. Since \( \Gamma_{\tau} \) is the ring of integers of \( \mathbb{Q}(\sqrt{-m}) \) which ideal class group of \( \mathbb{Q}(\sqrt{-m}) \) is trivial, \( k k_0 \Gamma_{\xi}^{S} \) is also a principal ideal of \( \Gamma_{\xi} \) and can be described as \( (k_0)(k) \), i.e., an ideal equation \( (k_0) \cap (k) = (k_0)(k) \) holds. Therefore, \( \xi = \tau \). This theorem is derived from a fundamental theorem in the algebraic number theory that If the ideal class group of algebraic number field \( K \) is trivial, all ideals of the ring of integers of \( K \) are principal ideal [17]. This fundamental theorem indicates that the symmetry of superstructure is determined by the structure of ideal class group that is an invariant in the algebraic number field.

III. APPLICATION OF LATTICE MATCHING THEORY TO 2D MATERIALS

The structure equation is also useful in structure analysis. When a superstructure is formed by placing an overlayer on a substrate, the structural analysis is made as follows: The symmetry and the unit cell of the superstructure are investigated by low-energy electron diffraction (LEED), scanning tunneling microscopy (STM) and etc. Possible structural models are counted, which are scrutinized by quantitative analysis such as dynamical LEED and the structure optimization with the total energy calculations based on density functional theory (DFT). In this process, (i) one constructs a trial model by tuning the lattice constant of the overlayer and rotating the overlayer relatively to the substrate to reproduce the superstructure. Then, (ii) the positions of atoms inside the unit cell of the trial model are fully relaxed and optimized in the quantitative analysis. This process is carried out repeatedly for various trial models and the most probable one is obtained. The step (i) is key in this routine to reach the probable model efficiently. Although the step (i) is usually carried out in the 2D vector space, this modeling involves the concerns as described in the introduction part. In contrast, the structure equation provides all the candidates to meet the overlayer symmetry. As described above, the equation \( (1) \), \( \gamma \Gamma_{\xi}^{S} \cap \rho \Gamma_{\sigma}^O = \gamma \Gamma_{\xi}^{S} \), holds for a superstructure \( \gamma \Gamma_{\xi}^{S} \) and an overlayer \( \rho \Gamma_{\sigma}^O \). We obtain the trial model when we determine \( \rho \) from \( \gamma \), \( \tau \) and \( \sigma \) which are known parameters. From the existence condition of solutions, \( \gamma/\rho \) can be described as \( \gamma/\rho = a + b \sigma \) where \( a \) and \( b \) are integers. We specify both \( a \) and \( b \) to meet the condition that \( |\rho| = |\gamma/(a + b \sigma)| \) is a reasonable value as the lattice constant of overlayer, and then we obtain a physically reasonable trial model.

As an example, let us consider a superstructure formed by placing a honeycomb structure on a substrate hexagonal lattice commensurately. This type of superstructure has been reported for graphene and silicene on metal substrates [6-11, 13, 14], and is generally described as \( \sqrt{n} \times \sqrt{n} R_{\phi \delta} \) relative to the substrate. This comes from the algebraic nature of the ideal class group of \( \mathbb{Q}(\sqrt{-3}) \) which is trivial group. According to the theorem, in the lattice groups of honeycomb overlayer \( \rho \Gamma_{\sigma}^O \), the
\( \delta = \lambda \) is the lattice constant of the substrate. Combined with layer and substrate lattices as shown in Fig. 3. To construct the model of superstructure, we must determine \( k \). Since \( k \in \Gamma_\omega \), \( k \) can be written as \( k = x\omega + y \), \((x, y) \in \mathbb{Z}^2 \setminus \{0,0\} \), which yields \( k = \sqrt{K_{xy}} e^{i\phi} \), where \( K_{xy} = |x\omega + y|^2 = x^2 + xy + y^2 = 1, 3, 4, 7, 9, 12, 13, 16, \ldots \) and \( \theta = \arg(x\omega + y) = \tan^{-1} \frac{xy}{x^2 + y^2} \). From the equation (2), \( k_0 = k_0 \lambda \) i.e., \( \sqrt{\mathbb{I} \exp(i\delta)} a_{\text{sub}} = \sqrt{K_{xy}} \exp(i\phi) a_{\text{sub}} \) is obtained. Finally, we obtain the equation which determines \( K \), i.e., pair(s) of \((x, y)\), as follows:

\[
a_h = \frac{\sqrt{n_{\text{sub}}}}{\sqrt{K_{xy}}} \theta = \phi_S - \delta. \tag{3}
\]

Although there are infinite candidates for \( K_{xy} \) to satisfy the equation (3), we can narrow \( K_{xy} \) down into a limited number of candidates because \( a_h \) must take a physically reasonable range as a lattice constant of honeycomb structure. In addition, \( K_{xy} \exp(i\theta) \) must meet another condition that \( K_{xy} \exp(i\theta) \) is coprime to \( \sqrt{n} \exp(i\phi) \) on the ring \( \Gamma_{\omega} \). Otherwise, there exists another superstructure specified with an integer smaller than \( n \). This condition comes from the ideal equation \((k_0) \cap (k) = (k_0)(k)\) (See the proof in Appendix). The algorithm to determine the structure model is summarized as a flowchart in Fig. 4.

Now, we construct the structural model of graphene that forms \( \sqrt{52} \times \sqrt{52} \) \( \Gamma_{13} \times \Gamma_{13} \) superstructure on \( \text{Pt}(111) \) [6,7] following the algorithm. This superstructure is so large that it is not easy to construct the structural model. However, we can obtain only one probable model by using the equation (3). Referring to the lattice constants of graphene \((a_h = 2.46 \text{ Å})\) and \( \text{Pt}(111) \) \((a_{\text{sub}} = 2.77 \text{ Å})\), the equation (3) yields \( K_{xy} = 64, 67 \) and 73 as suitable candidates. If \( K_{xy} < 64 \), then \( a_h > 2.51 \) \((a_h < 2.34)\), which is too large (small) as a lattice constant of graphene. Among \( K_{xy} = 64, 67 \) and 73, \( K_{xy} = 64 \), does not satisfy the condition that \( K_{xy} \) is coprime to \( n \) so that the structure model for \( K_{xy} = 64 \) is ruled out. Figure 5(a) shows the structural model of \( K_{xy} = 64 \). Indeed, the model is not \( \sqrt{52} \times \sqrt{52} \) \( \Gamma_{13} \times \Gamma_{13} \) but \( \sqrt{13} \times \sqrt{13} \) \( \Gamma_{13} \times \Gamma_{13} \). In contrast, both \( K_{xy} = 67 \) and \( K_{xy} = 73 \) satisfy the coprime condition. The lattice constant derived from \( K_{xy} = 67 \) is 2.44 Å which is nicely matched with \( a_h = 2.46 \text{ Å} \), while 2.34 Å obtained from \( K_{xy} = 73 \) is shorter. Thus, the model for \( K_{xy} = 67 \) is better than that for \( K_{xy} = 73 \). Figure 5(b) shows the structural model of \( \sqrt{52} \times \sqrt{52} \) graphene derived from \( K_{xy} = 67 \). As shown in Fig. 5(b), this model nicely reproduces the moiré pattern observed by Gao et al. [7] and the structure models proposed by theoretical analysis [8, 18-20]. These examples clearly show that the notion of the lattice group and the structure equation are powerful in the structure analysis.

IV. SUMMARY

In summary, we built up a theory on the lattice matching condition of two 2D lattices based on algebraic number theory. By mapping 2D Euclidean space to complex plane, we derived a theorem on lattice matching condition that cannot be derived by 2D vector analysis. Utilizing the theory, we demonstrated an algorithm to construct a structure model which was successfully applied to graphene on \( \text{Pt}(111) \).

ACKNOWLEDGMENTS

This work was partially supported by JSPS KAKENHI Grant Number 24241040 and by MEXT KAKENHI Grant Number 25110008.
Here, we show a proof of the coprime condition that $k_0$ is coprime to $k$ on the ring $\Gamma_\omega$ from the ideal equation, $(k_0) \cap (k) = (k_0)(k)$.

Proof. Let the greatest common divisor of $k_0$ and $k$ be $a \in \Gamma_\omega \setminus \{0\}$. Then $p, q \in \Gamma_\omega \setminus \{0\}$ exist such that $k_0 = ap$ and $k = aq$. Thus, $(k_0) = (a)(p)$ and $(k) = (a)(q)$ hold. Then we obtain $(a)(p) \cap (a)(q) = (a^2)(p)(q)$. $(a)(p)(q) \subset (a)(p)$ and $(a)(p)(q) \subset (a)(q)$ are obvious. Thus, $(a)(p)(q) \subset (a)(p) \cap (a)(q) = (a^2)(p)(q)$ holds. Since $(a^2)(p)(q) \subset (a)(p)(q)$ is obvious, we obtain $(a^2)(p)(q) = (a)(p)(q)$. Therefore, $a$ is the unit of the ring $\Gamma_\omega$. Q.E.D.