



# Manipulation of Dirac cones in intercalated epitaxial graphene



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## ABSTRACT

Graphene is an intriguing material in view of its unique Dirac quasi-particles, and the manipulation of its electronic structure is important in material design and applications. Here, we theoretically investigate the electronic band structure of epitaxial graphene on SiC with intercalation of rare earth metal ions (e.g., Yb and Dy) using first-principles calculations. The intercalation can be used to control the coupling of the constituent components (buffer layer, graphene, and substrate), resulting in strong modification of the graphene band structure. It is demonstrated that the metal-intercalated epitaxial graphene has tunable band structures by controlling the energies of Dirac cones as well as the linear and quadratic band dispersion depending on the intercalation layer and density. Therefore, the metal intercalation is a viable method to manipulate the electronic band structure of the epitaxial graphene, which can enhance the functional utility and controllability of the material.

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## 1. Introduction

Graphene, a two-dimensional atomically thin layer of carbon, has been one of the most attractive material candidates for future electronics [1–4]. The distinctive low-energy electronic structure of graphene, the “relativistic” Dirac cone, has been of profound importance from both fundamental and practical points of view [3–8]. By virtue of its low dimensionality, the electronic properties of graphene can be effectively changed via physical or chemical coupling to neighboring components, e.g., substrate or adjacent graphene layers. For instance, epitaxial graphene on SiC, which is one of the most successful ways to realize large-scale few layer graphene [7,9–12], is a notable example where the substrate has a crucial effect on the electronic structure of the graphene. Also, different stacking in few layer graphene results in different band structures [13]. Thus, the coupling to the nearby layers is important to understand the electronic structure of graphene. In this regard,

intercalation is a promising way to change the coupling among the graphene layers and the substrate. Recently, the intercalation of epitaxial graphene has become a realistic and robust route to control the physical and chemical properties of the graphene [14–18], e.g., the chemical adsorption properties [16] and the quasi-particle excitation [15,18–21]. Also, there are previous theoretical studies of intercalated epitaxial graphene which demonstrate different types of modifications to the band structure: Dirac cones [22], Dirac half metal [23], and gate-independent energy gap [24].

Although the intercalation has been a promising avenue to affect graphene properties (the number and type of charge carriers, nucleation of new phases on top, magnetic properties, etc.), it is still not clear what determines the optimal conditions (i.e., temperature, annealing time, type of substrate graphene is deposited on) which are needed for a given element to intercalate graphene. There have been experimental investigations regarding important issues such as Fermi level shift [14,19,20] and decoupling of the buffer layer [14,15,18–21]. However, these experiments are based on ARPES measurements of the final state generated after thermally annealing, and there is no stepwise control of the growth parameters to monitor intermediate phases, the intercalated morphology and the atom distribution within the intercalated layer. Intercalation is a much more complex process with important questions related to kinetics and thermodynamics describing the

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different phases with distinct properties that can form below graphene. In this regard, first-principles electronic structure calculations are essential to find out a variety of possibilities in the electronic band structure facilitated by intercalation. Furthermore, they provide key information about the intercalation configuration in that they predict the band structure as a function of experimental parameters: the amount of dopant, the location of the dopant whether at the buffer-SiC interface or buffer-monolayer interface, and changes from the normal AB to AA graphene stacking.

In this study, we demonstrate that the electronic band structure of graphene, epitaxially grown on Si-terminated SiC, can be controlled by metal intercalation using first-principles calculations based on density functional theory (DFT). We consider intercalation of rare earth (RE) metal atoms (Yb, Dy) in the epitaxial graphene, and show that the intercalation can strongly modify the electronic band structure of the system by effectively decoupling the constituent components: substrate, buffer layer, and graphene layer. As a result, we can obtain decoupled linear Dirac bands as well as quadratic bands depending on the configuration of the intercalation. In addition, the intercalation density significantly affects the electron filling and screening, and hence the energies of the Dirac points with respect to the Fermi level change accordingly. These diverse opportunities for different band structures by the intercalation would provide practically useful routes to manipulate the electronic structure of the epitaxial graphene. We also discuss the intercalation configuration in the recent Yb intercalation experiment.

## 2. Theoretical methods

The electronic structures were calculated using DFT as implemented in VASP package [25,26]. We employed a plane-wave basis set with a cutoff energy 400 eV, and the interaction between ions and valence electrons was described by exploiting the projector-augmented wave method [27]. We used 2 layers of SiC for the Si-terminated substrate with  $2\sqrt{3} \times 2\sqrt{3}R30^\circ$  supercell, which can accommodate  $4 \times 4$  graphene layers on top of it. The lattice constant of SiC was adjusted by approximately 7.8% to match that of the  $4 \times 4$  graphene layer. Although epitaxial graphene may have the  $6\sqrt{3} \times 6\sqrt{3}R30^\circ$  superstructure experimentally, our calculations are supposed to capture the essential features since our main focus is the graphene band structure after the buffer layer is decoupled from the SiC substrate by the metal intercalation. The Perdew-Burke-Ernzerhof exchange-correlation functional was adopted [28], and the van der Waals energy was accounted for using the DFT-D3 method [29].  $6 \times 6 \times 1$   $k$ -point mesh was used.

## 3. Results and discussion

In epitaxial graphene, the interaction with a substrate is essential to understand the electronic band structure. The initial carbon monolayer on Si-terminated SiC has strong chemical hybridization with the substrate Si, and it is called a buffer layer (or the 0th graphene layer). In terms of the electronic band structure, the buffer layer does not possess a Dirac cone due to the chemical bonding with the substrate, unlike the free-standing graphene [15,20]. Additional Si desorption can induce a new buffer layer to form at the SiC interface, causing the previous buffer layer to transform into the 1st layer of graphene which acquires a Dirac cone.

The main character of the graphene band structure, i.e., the Dirac dispersion of the  $\pi$  bands, can be recovered in the buffer layer if we can change the chemical interaction between the buffer layer and the substrate. Recent experimental literature shows that the

intercalation can effectively decouple the buffer layer from the SiC substrate as demonstrated by the appearance of the Dirac cone of the decoupled buffer layer [15,18–21]. For example, the intercalation of Ge, Au, H has been shown to induce the decoupling of the buffer layer from the substrate [15,19,20], recovering the Dirac cone in the buffer layer. Also, the chemisorption of graphene on a metallic substrate and the appearance of the Dirac cone, e.g., under Au intercalation is reported on Ni(111) [30], and under oxygen intercalation on Ru (0001) [31].

Here, we consider two different intercalation layers (Fig. 1), i.e., upper and lower intercalation layers for the RE intercalation. The lower intercalation layer denotes the intercalation layer beneath the buffer layer, which can be utilized to control the coupling between the buffer layer and the outermost Si layer of the SiC substrate. The upper intercalation layer corresponds to the intercalation on the buffer layer, and it is expected to affect the interaction between the graphene and the buffer layer. According to the recent experiment, the intercalation can occur in the lower intercalation layer [18]. The intercalation in the upper intercalation layer could also happen depending on the experimental conditions and preparation methods because rare-earth-intercalated bulk graphite exists experimentally although the intercalation conditions are different from pathways possible under UHV [32]. Also, there is an experimental report for Au intercalation between the buffer and the graphene layers [33,34]. As will be shown below, the upper layer intercalation is useful for the manipulation of the Dirac cones in the graphene layers.

We first consider the Yb intercalation of epitaxial graphene. If the lower intercalation layer is filled, the two carbon layers form a bilayer graphene on the substrate. In Fig. 2, the atomic and electronic structures of Yb-intercalated epitaxial graphene are presented (only the band structure for one spin polarization is shown, since that for the other spin is essentially similar in view of the Dirac cones in the graphene layers). Here, we assume  $2 \times 2$  intercalation (i.e., one Yb atom in  $2 \times 2$  unit cell in terms of the graphene layer) and AB-stacking of the bilayer graphene. Due to the electric potential gradient from the substrate and Yb intercalation layer, the bilayer graphene has different onsite energies in the top and bottom graphene layers, and hence the electronic band structure shows two Dirac cones having different energies. Also, owing to the AB-stacking of the two carbon layers, the two Dirac cones have quadratic dispersion with strong hybridization between them (Fig. 2c and d), as expected in the bilayer graphene under external electric fields or pristine bilayer graphene on a substrate [9,35–37]. Although some hybridizations with other bands also occur (Fig. 2c) to change the detailed dispersion, the overall shape of the bands from the graphene and the decoupled buffer layer follows that of bilayer graphene under external fields. In general, the band structure and the band gap can be affected by the interaction with the intercalation layer and substrate or by the vertical electric fields from them [24].

The intercalation in the upper intercalation layer as well as the lower one has a significant effect on the electronic band structure in terms of the energies of the Dirac points and the coupling between the two layers. There are three major effects of the upper layer intercalation on top of the lower layer one. i) The relative stacking of the bottom graphene layer (i.e., the decoupled buffer layer) and the top graphene layer becomes AA rather than AB. ii) The energy of the Dirac cone in the top graphene layer downshifts with respect to the Fermi level  $E_F$  because of the electron transfer from the upper Yb intercalation. iii) The screening of the electric fields by the upper Yb layer changes the relative energy separation of the two Dirac points. These can be seen by comparing the two cases, i.e., with and without the upper layer intercalation (Fig. 3b and Fig. 2c). After the upper layer intercalation, we note that there appear two linear

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