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Interfacial topography and properties of graphene sheets on different reconstructed silicon surfaces

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ABSTRACT

Graphene growth on a substrate has been widely investigated due to its broad application potential. Previous studies have found that the properties of graphene depend on its underlying substrate and their interaction. However, the dynamic behavior of the interfacial structure as a function of temperature has not been investigated, as well as the interfacial structure related to its mechanical properties. In this work, molecular dynamics has been employed to study the topographic characteristics and intrinsic mechanical properties of graphene when attached to a reconstructed silicon surface. The fitness between the interfacial structures plays an important role in stabilizing the attached graphene and forming pattern. The degree of planarity of the attached graphene determines the magnitude of the residual stress, while temperature affects atomic bonding and varies this residual stress. Findings suggest that the different pairings between graphene and surface structures significantly affects the topographic characteristics, residual stress, and interaction strength of the graphene sheet, which would further change the electronic properties of its application.

1. Introduction

Graphene is perhaps one of the most promising materials ever discovered for microelectronics applications, because it has many excellent mechanical, thermal, electronic, and optical properties. However, despite its intriguing properties, one of the biggest hurdles is the fact that graphene is intrinsically a zero bandgap semiconductor. Its valance and conduction bands are cone-shaped and meet at the K points of the Brillouin zone. The lack of bandgap constrains the application potential in electronic materials. As a result, many past studies have focused on the modification of the electronic properties (e.g., bandgap, Fermi level, and work function) of graphene. The methods developed to adjust the bandgap of graphene include constraining the size of graphene in one dimension to form a nanoribbon [1], applying biasing to bilayer graphene [1], applying strain to graphene [1], and hetero atom doping [2]. In addition, Graphene has been found to have a negative thermal expansion coefficient (TEC) due to the competition between the in-plane expansion and out-of−plane fluctuation of graphene [3] and has a transition temperature (the temperature at which the TEC reverses from negative to positive) that differs with methodology: around 350 K as determined by experiment [4], at 900 K as determined by quasiharmonic approximation [5], at 2500 K by first principles calculation [6] and at 600 K by Green's function method [7]. However, TECs of graphene as measured by Yoon et al. was always negative between 200 and 400 K. Since the transition temperature of TEC of graphene is still not clear, as was mentioned, the quantitative discrepancies remain to be resolved by more accurate experimental measurements.

Besides the single graphene sheet, graphene growth on a substrate has been widely investigated. There are several ways to produce graphene on a substrate, such as liquid phase and thermal exfoliation, chemical vapor deposition (CVD), and epitaxial growth. The epitaxial growth method is a high-temperature growth approach which is dependent on the substrate material, which is difficult to alter. However, exfoliation and CVD approaches enable the transfer of graphene to different substrates [8,9]. This makes it possible for modify the properties of graphene by transferring it

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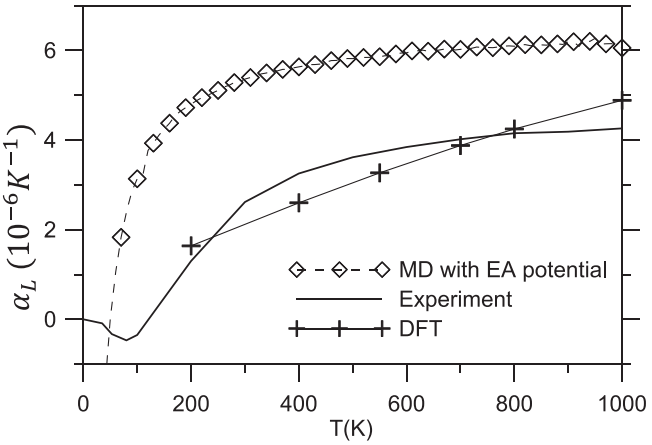

Fig. 1. Linear TEC of silicon crystal obtained by our MD simulation, by experiment [41] and by DFT [42].

onto different substrates [10]. Past studies have also found that the bandgap in the graphene can be opened and modulated by the surface chemistry of the different supporting substrates [11–14]. In addition, graphene covering different substrates can have different Schottky barrier heights [10], and this height can be controlled by adjusting the gate voltage [15]. These characteristics can attributed to the covalent bonding and charge transfer between the graphene and substrate. Similarly, the graphene can attach to the substrate by the weak van-der Waals interaction due to the surface hydrogenation of the substrate [8,12,16], such that it can retain its intrinsic properties. Alternatively, this can occur in bilayer graphene [12,16], where the bottom layer acts as a buffer layer to isolate the upper layer. Due to these unique properties explained above, as well as its thin one-atom thickness and its tuning ability, graphene/substrate heterojunctions have been recognized as promising candidates for new-generation diodes [10], solar cells [17], logic transistors [15], and energy-harvesting devices [18].

Understanding the topographic characteristics of graphene and its interaction with the supporting substrate, therefore, is crucial for further development of nanoelectronic devices. Previous experimental and theoretical research of graphene covering SiC [19], SiO_2 [12,16], and Si [8,20] substrates shows that the strong interaction between graphene and its substrate weakens C–C bonds in the graphene plane and causes the formation of partial *sp*3 hybridization in the graphene, which then soften phonons of the graphene layer [21]. The property of graphene depends on which site it is located and on what substrate it is deposited. On the oxygen polar surface of silicon dioxide (SiO_2) [12], graphene exhibits semiconductor behavior due to the charge transfers of oxygen to the graphene, which induces p-type graphene and an n-type surface. On the SiO_2 silicon polar surface [12], Si(100)2 × 1 [8], it remains metallic in its behavior, resulting in n-type graphene and p-type surface. However, on a hydrogen terminated surface [8,12,16], graphene can freely stand on the surface. No charge transfer between graphene and the substrate is observed, its band structure consistent with isolated graphene. The structural characteristic of the substrate surface also plays an important role to alter the interaction between graphene and the substrate. For example, the Si(111)7 × 7 surface with unterminated bonds at the dimer and adatom behave extremely reactively and have different charge distributions [9]. Scanning tunneling spectroscopy (STS) measurements suggest that the graphene-substrate bonding is relatively strong [20]. The graphene covering the reconstructed oxygen polar surface of SiO_2 substrate [16] exhibits intrinsic metallic behavior rather than semiconductor as mentioned above [12] due to no charge transfer at the interface.

In terms of its topographic property, graphene on the SiC surface has been studied by molecular mechanics, with an obvious regular and periodic pattern appearing on the graphene due to the variation in topography [19]. Graphene on a metal crystal surface

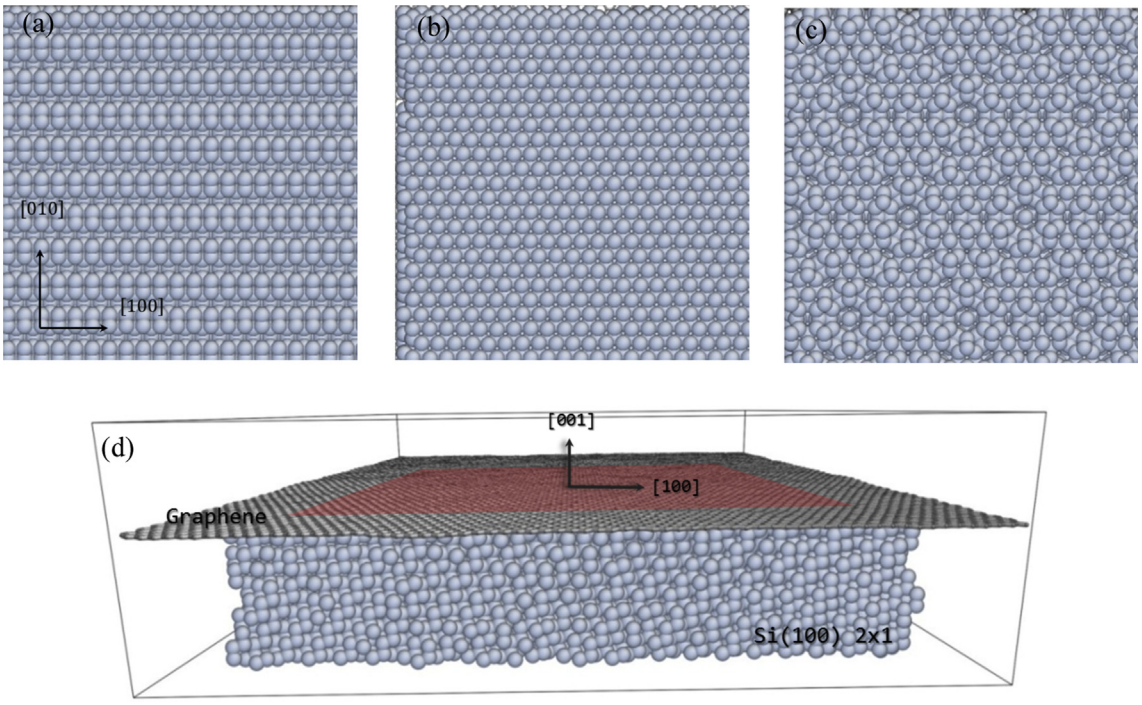

Fig. 2. Simulation models of (a)Si(100)2 × 1, (b)Si(111)1 × 1, and (c)Si(111)7 × 7 reconstruction surfaces. (d) The combined model of graphene and Si(100)2 × 1 substrate(Gr/Si(100) 2 × 1). The frame in red illustrates the range of collected simulation data. (A color version of this figure can be viewed online.)