Intercalation of Kr atoms into Graphene on SiC(0001)

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Graphene, a two dimensional hexagonal form of carbon atoms, is attracting a great interest since its experimental finding in 2004. Because the carries, both electrons and holes, in an ideal graphene sheet behave like the massless Dirac fermions, it exhibits a series of new electronic properties such as the anomalously quantized Hall effects, the absence of weak localization, and the existence of a minimum conductivity. In addition, the sp2 bonding of carbon atoms makes it chemically inactive and mechanically robust and flexible. Therefore, Graphene can be an excellent candidate for the next generation of electronic materials. A next step of the graphene research is to find ways to control its physical properties. One of the strategies is to functionalize graphene by depositing atoms or molecules on graphene. For example, it is well known that some adsorbates transfer either electrons or holes into graphene and change the conductance at fixed gate voltage, which can result graphene in a gas sensor. In the case of alkaline atoms as adsorbates, the amount of transferred charge is so much that the Fermi energy (E_F) can reach to the saddle point, the van Hove singularity, which can even lead the superconducting instability. The superstructure of adsorbates, on the other hand, can modify the electronic interaction in graphene which can result in the band gap opening. The chiral symmetry breaking and resultant band gap opening is expected when the adsorbates form ($\sqrt{3}$x$\sqrt{3}$)R30° structure.

Here, we report on the effect of Kr atoms deposited on graphene epitaxialy grown on SiC(0001). It is well known that most rare gas atoms adsorb on the surface of graphite in layer-by-layer and form two dimensional (2D) solid. At lower densities, they are adsorbed on the hollow site of the honeycomb lattice of graphite to form ($\sqrt{3}$x$\sqrt{3}$)R30° phase.

The surface topography and electronic states of graphene on SiC(0001) are studied with our home designed scanning tunneling microscope, named the ULT-STM, which can work in multi-extreme conditions, i.e. at temperatures down to 30 mK, in high magnetic fields up to 13 T and in ultra-high vacuum (UHV) [1]. The chamber for the microscope is directly connected to the UHV chambers at room temperature, where one can prepare and evaluate the samples and tips for STM. The prepared samples and tips can be transferred to the microscope at T ~ 2 K *in-situ* in UHV quickly within a minute, afterwards the STM with newly installed sample and tip can be cooled down to the base temperature within a few hours.

Kr atoms were deposited onto graphene in a UHV chamber by keeping the temperature of graphene substrate and the partial pressure of Kr for certain time duration (10 minute, in this study). This way of sample preparation worked well in our setup for Kr atoms on graphite [2], where the relation between temperature and saturated vapor pressure of 2D Kr solid had been studied well in various experiments. In the case of graphene as a substrate, however, the P-T phase diagram should be modified reflecting the difference of the adsorption energy of Kr on either graphite or graphene. In general, the adsorption energy on graphene is smaller than that on graphite, and lower temperature or higher pressure is necessary to form the 2D Kr solid on graphene than on graphite. In this study, we have prepared two samples with different areal densities. The sample #1 was prepared at $T = 42 \pm 0.3$ K and $P = (8.7 \pm 0.3) \times 10^{-8}$ Pa, while sample #2 at $T = 35 \pm 0.05$ K and $P = (7.2 \pm 0.3) \times 10^{-8}$ Pa, which means that the density of Kr on sample #1 is smaller than that on sample #2.

As the graphene substrate, monolayer and bilayer graphene epitaxially grown on 6H-SiC(0001) is adopted [3]. It is well known for graphene on SiC(0001) that there is a C-rich buffer layer with 6x6 corrugation in between graphene sheet and the SiC(0001) surface. Because of this buffer layer, graphene sheet shows the 6x6 corrugation together with the honeycomb lattice of C in STM images. The 6x6 corrugation of the surface is getting weaker for thicker graphene when the surface layer is away from the buffer layer. In the I-V spectroscopy, on the other hand, the Dirac point (E_D) is observed at negative voltages as a dip in the dI/dV spectrum suggesting that electrons are doped to graphene from the substrate. And the E_D is getting closer to the Fermi energy (E_F), i.e. zero bias voltage, for thicker graphene.

Throughout this study, we have focused on around a boundary between mono- and bi-layer graphene. In this study, a boundary of lower and upper terraces is observed with the height difference of 0.16 nm

(figure 1(a)), which is about half of interlayer distance of graphite. The 6x6 corrugation of lower and upper terraces are 18 pm and 9 pm, respectively, suggesting that the lower (upper) terrace is mono- (bi-) layer of graphene [4]. The dI/dV spectrum shows a dip feature at -175 mV for lower terrace, while such dip feature is observed at 30 mV higher energy for upper terrace. Though the absolute energies of the dip feature are different from other studies [4], this change of the dip energy depending on the terraces suggests that the upper terrace is thicker than the lower.

When Kr atoms are deposited on graphene on SiC(0001), no Kr atoms are observed on the surface. It is surprising difference from the behavior on graphite, where each Kr atoms could be observed clearly with STM [2]. However, it does not mean that Kr atoms are not deposited on the graphene sample because some electronic properties are modified by Kr deposition as are discussed below and more during the conference. From the experimental results, one can expect that the Kr atoms are intercalated in graphene or buffer layer instead of adsorbing on the surface.

The effect of the Kr atoms is observed in four measurements. First, it is observed in the amplitude of the 6x6 corrugation. The corrugation is increased to 26 pm and 33pm for lower density sample (#1) and higher density sample (#2), respectively, on monolayer terrace. On the other hand, it is increased to 21 pm and 44 pm for sample #1 and #2, respectively, on the bilayer terrace. The corrugation is increased monotonically by increasing the amount of Kr atoms. This finding suggests that the intercalated Kr atoms are adsorbed commensurate to the 6x6 corrugation of the buffer layer rather than to the honeycomb lattice. It is worth noting that the magnitude correlation of 6x6 corrugation between monolayer and bilayer terraces is reversed for higher Kr density sample (#2).

Figure 1 shows the change of the step height by depositing Kr atoms. It is doubly increased to 0.37 nm for sample #1 (figure 1(b)) from 0.16 nm for the bare graphene (figure 1(a)). Interestingly, the single step is split into two for sample #2, the higher Kr density sample (figure 1(c)). Each step height is 0.23 nm and 0.16 nm, here, the smaller step height is the same as that on the bare sample, and the total height difference is the same as that on sample #1.

The effect of Kr atoms is also observed in I-z spectroscopy. Because the tunnel current is exponentially changed by the distance between the surface and the STM tip, one can extract the decay length of the surface wave function to vacuum from the slope of the I-z relationship. Moreover, one can also deduce the work function from the decay length. In this study, it is observed that the slope of the I-z spectrum on bilayer terrace is steeper than that on monolayer terrace. And the slopes become smoother by increasing Kr density. Considering roughly that the slope is proportional to the work function of the surface, the results suggest that the work function is smaller on monolayer than bilayer, and smaller on higher Kr densities than on lower densities. This tendency that the work function becomes smaller by graphene intercalation is consistent to the study in reference [5].

Finally some changes of the surface DOS are also observed in the dI/dV spectrum. The dip feature in surface DOS is disappeared by the Kr intercalation. It can be because the graphene layers are electronically decoupled from the substrate and E_D is located close to the E_F. However, some theoretical approaches are necessary for better understanding.

The detail of these effects will be discussed in the conference.

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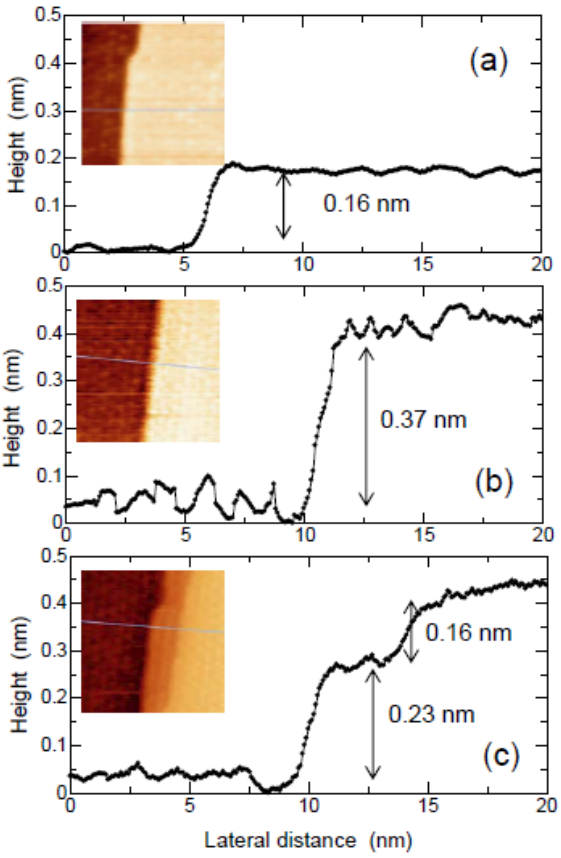

Figure 1. STM images (20 x 20 nm^2) and their line profile (along the line inside STM images) of (a) bare graphene, (b) sample #1 and (c) sample #2. The STM images show the boundary of lower monolayer terrace (left) and upper bilayer terrace (right).