Structure of Superconducting Ca-Intercalated Bilayer Graphene on SiC Studied using Total-Reflection High-Energy Positron Diffraction (TRHEPD)

We have investigated the atomic structure of superconducting Ca-intercalated bilayer graphene on a SiC(0001) substrate using total-reflection high-energy positron diffraction (TRHEPD). By comparing the experimental rocking curves with those calculated for various structural models using a full-dynamical theory, we have found that Ca atoms are intercalated in the graphene-buffer interlayer, rather than between the two graphene layers. This study is the first to clearly identify the relation between the atomic arrangement and superconductivity in Ca-intercalated bilayer graphene.

Graphene, a single atomic sheet of graphite, has attracted much interest for its remarkable properties such as massless charge carriers and quantum Hall effect caused by unique electronic structures. Furthermore, superconductivity induced in graphene has been a major focus [1, 2], and much effort has been made to fabricate superconducting graphene by investigating the results of metal doping, following observation of the effect in bulk graphite intercalation compounds (GICs). Ca-intercalated bilayer graphene on SiC substrate, which was regarded as the thinnest C_6Ca superconductor, has also been studied. An indication of superconducting transition was reported, where it was observed that the resistance dropped steeply at 4 K, reaching zero at 2 K [2]. It had been thought that Ca atoms were intercalated between bilayer graphene by analogy with the structure of bulk C_6Ca. There was, however, no direct evidence of the exact location of the intercalated-Ca atoms because bilayer graphene grown on a SiC(0001) substrate had a buffer layer beneath the graphene layers. To completely understand the superconducting mechanism of this compound, a comprehensive structural analysis with atomic resolution is required.

In this report, we demonstrate the results of investigating the atomic structures of Ca-intercalated bilayer graphene on SiC(0001) showing superconducting transition using total-reflection high-energy positron diffraction (TRHEPD) [3]. By comparing rocking curves calculated for various structural models with experimental data, we found that the Ca atoms are intercalated between the graphene layer and the buffer layer, and not between the two graphene layers, as shown in Fig. 1.

TRHEPD experiments were performed at the SPF-A3 [4]. TRHEPD is a highly surface-sensitive technique because it utilizes the property of positive electrostatic potential in every material. The rocking curve, which here is (00) spot diffraction intensity measured as a function of the glancing angle (θ), was extracted from a series of the TRHEPD patterns. The glancing angle was varied from 0.5° to ~6° at 0.1° intervals by rotating the sample. We minimized the difference between the measured rocking curves and the calculated rocking curves by optimizing the assumed structures, using a reliability factor *R* [5] as an index for degree of fit (smaller value of *R* indicates better fit).

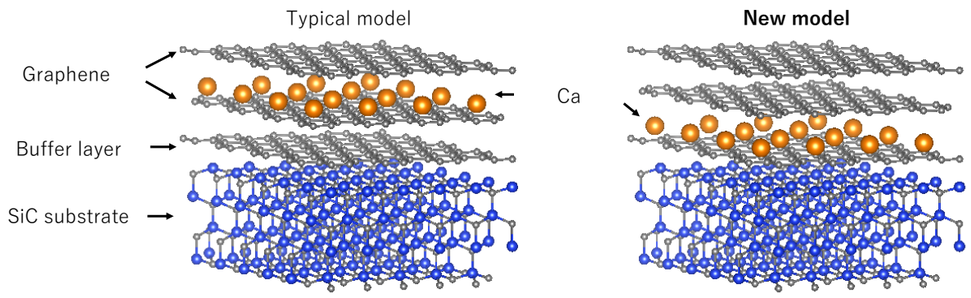

Figure 1: Comparison of the structure models of Ca-intercalated bilayer graphene on SiC(0001) between a typical conventional model (left) and the new model (right) determined by this study.

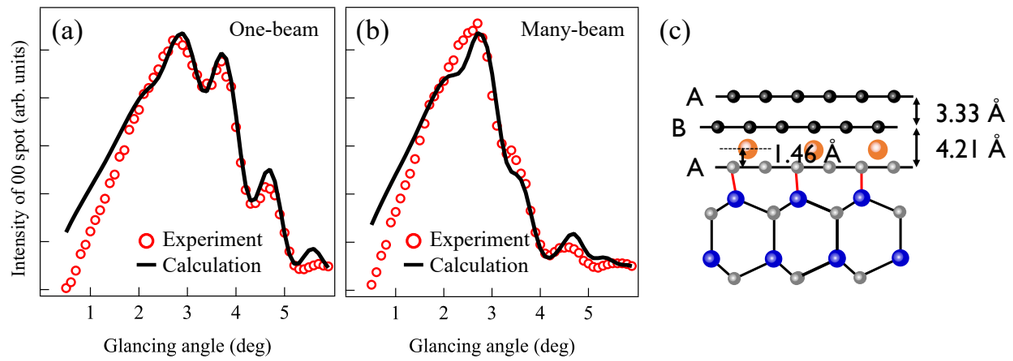

Figure 2: TRHEPD rocking curves under the (a) one-beam condition with calculated curves and (b) the many-beam condition with the calculated curves for Ca-intercalated graphene on SiC(0001). (c) Schematic view of the structure determined for Ca-intercalated graphene on SiC(0001).

Figure 2(a) shows the rocking curves of the Ca-intercalated bilayer graphene under the one-beam condition, which essentially includes the information of spacing in the out-of-plane direction only. The black solid line in Fig. 2(a) has the best agreement with the experimental curve (R ~1.43%). Next, rocking curves under the many-beam condition which includes information on the in-plane structure as well as on the out-of-plane structure were analyzed. Namely, we can denote the stacking sequence including the locations of Ca atoms from the bottom to top layers. Figure 2(b) shows the experimental and calculated rocking curves for the Ca-intercalated bilayer graphene under the many-beam condition. Finally, we summarized the structures determined in this study of Ca-intercalated bilayer graphene on SiC(0001) as shown in Fig. 2(c). The interlayer distances were obtained as follows: the graphene-buffer spacing is 4.21 ± 0.11 Å and that of graphene-graphene is 3.33 ± 0.16 Å. The Ca atoms are located in the graphene-buffer interlayer, 1.46 ± 2.24 Å above the buffer layer. Our result indicates that the Ca atoms are intercalated in the graphene-buffer interlayer only. Moreover, we found that the Ca-intercalated interlayer distance is close to that of the bulk C_6Ca (~4.5 Å) and Ca atoms are located at the center of hexagonal lattices of the buffer layer. For the bulk C_6Ca, it is known that the intercalated Ca atoms form a $\sqrt{3}\times\sqrt{3}$ periodic structure and the carbon layers align in AA stacking. However, the "A-Ca-BA" (R ~1.70%) stacking sequence was found to give the best agreement with the experimental data, being more plausible than the "A-Ca-AB" stacking. The result suggested that no stacking shift from the pristine one occurred on the Ca-intercalation.

This result is a significant step in elucidating the superconducting mechanism of Ca-intercalated bilayer graphene on SiC. Furthermore, the study suggests the possibility of superconductivity in monolayer graphene on SiC since it has been found that the contribution of the top graphene layer to this property may be negligible. It is also expected that Ca-intercalated monolayer graphene can be a system where superconductivity and Dirac electrons can coexist.

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BEAMLINE

SPF-A3

Y. Endo[1], Y. Fukaya[2], I. Mochizuki[3], A. Takayama[4], T. Hyodo[3] and S. Hasegawa[1] ([1]The Univ. of Tokyo, [2]JAEA-ASRC, [3]KEK- IMSS, [4]Waseda Univ.)