Structure determination of Ca-intercalated bilayer graphene by positron diffraction

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Recently, bilayer graphene, which is stacked by two graphene layers, was found to undergo superconducting transition at around 4 K due to Ca intercalation [1]. Because of being regarded as thinnest superconductor, bilayer graphene superconductor has attracted increasing attention. In Ca-intercalated bilayer graphene, charge transfer from Ca atoms is the key to possess the superconducting transition. In the analogy of graphite intercalation compounds (GICs), Ca atoms were expected to be intercalated between two graphene layers. However, the atomic arrangement, in particular, Ca sites, remained unresolved. In this study, we investigated the atomic arrangements of Ca-intercalated bilayer graphene synthesized on a SiC(0001) substrate using total-reflection high-energy positron diffraction (TRHEPD) technique [2].

TRHEPD is a surface sensitive tool owing to the positive charge of positrons, opposite to electrons [3,4]. When striking a crystal surface, the positron beam feels a repulsive force due to the electrostatic potential composed of a nucleus and surrounding electron clouds. Thus, the penetration depth of positron beam into crystal becomes considerably limited. Especially, total reflection occurs at grazing angles, where the penetration depth corresponds to the thickness of one atomic layer. Therefore, TRHEPD is suitable to determine the atomic arrangements of two-dimensional materials such as graphene.

As a result, we found that Ca atoms are intercalated in the interface between bilayer graphene and SiC(0001) substrate, not in the bilayer graphene. We synthesized the bilayer graphene on a SiC(0001) substrate through a standard thermal decomposition method, followed by the intercalation of Ca atoms in a ultra-high vacuum chamber. We measured rocking curves, diffraction spot intensity versus the glancing angle of incident positron beam, for the Ca-intercalated bilayer graphene (Fig. 1(a)). Three prominent peaks (2.8°, 3.7° and 4.6°) in the curve are identified. In order to seek the optimum structure, we performed intensity calculations on the basis of dynamical diffraction theory. We assumed three different atomic arrangements for plausible structure models; Ca atoms are intercalated (#1) between the bilayer graphene layers, (#2) between the bilayer graphene and the SiC(0001) substrate, and (#3) in the both. Only the curve calculated using the structure model #2 (denoted as red line in Fig. 1(a)) is in good agreement with the measured one. The spacing between the bilayer graphene and the SiC(0001) substrate is expanded by approximately 1 Å due to Ca intercalation (Fig. 1(b)). Whereas, there is no change in the interlayer spacing in the bilayer graphene layers, which is nearly the same as that for graphite. Our result differs from the prior prediction based on GICs studies, in which the Ca atoms are intercalated between the bilayer graphene layers.

We also confirmed using four-point probe measurements that the superconducting transition occurs at around 4 K for our sample of Ca-intercalated bilayer graphene (Fig. 1(c)).

Our findings will stimulate the reinterpretation of the superconducting transition mechanism for graphene. Furthermore, it might lead to the realization of single-layer graphene superconductor.

References
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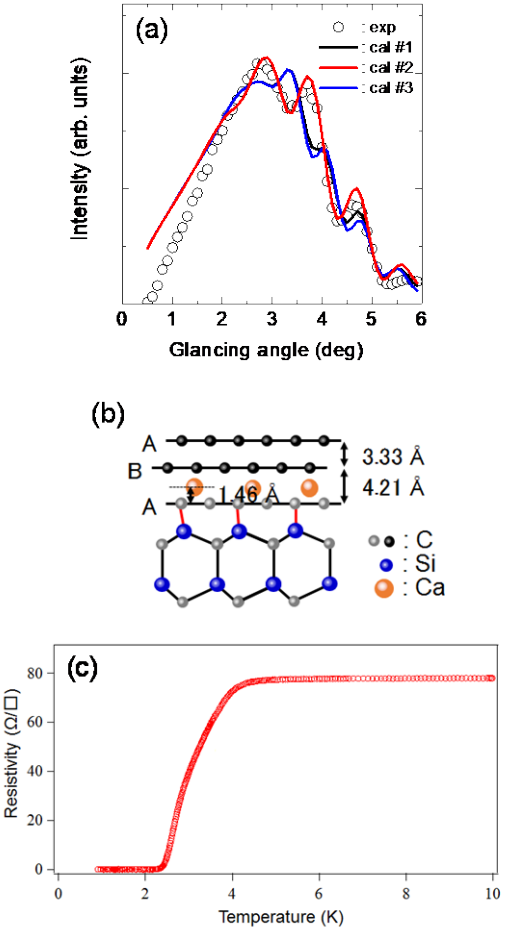

Fig. 1 (a) TRHEPD rocking curves for Ca-intercalated bilayer graphene on a SiC(0001) substrate. The beam energy is set at 10 keV. Open circles indicate the measured curve and solid lines are the calculations using various structure models (#1-#3). (b) Best-fitted structure model obtained in this study. (c) Temperature dependence of the resistivity for Ca-intercalated bilayer graphene.