Interface Structure between Graphene and Metal Substrates Determined by Total-Reflection High-Energy Positron Diffraction (TRHEPD)

We have investigated the interface structure between graphene and metal substrates using the total-reflection high-energy positron diffraction (TRHEPD) technique. The spacing between the graphene and a Co(0001) substrate is determined to be 2.06 Å whereas that for a Cu(111) substrate is 3.34 Å. The former indicates the formation of chemical bonds between the Co and C atoms. The latter indicates weak interaction with the Cu substrate due to the Van der Waals force.

Recently, graphene is attracting much attention because of its extremely high carrier mobility and many other promising features such as high thermal conductivity and robust mechanical properties. The contact of graphene with other materials brings about significant changes in its properties. For example, the calculated electronic band structures of graphene on Al(111) and Pt(111) substrates exhibit the existence of the Dirac cone while that for Co(0001) substrate does not [1]. Moreover, theoretical calculations demonstrate that the electronic structure of graphene is closely related to the interface structure, especially the spacing between graphene and the metal substrate [1]. Therefore, determination of the spacing between graphene and the substrate is crucial to elucidate the origin of the electronic property of graphene adsorbed on the metal substrate. However, the spacing had not been investigated experimentally, except for the case of an Ni substrate. In this study, we determined the spacing between graphene and substrates of Co(0001) and Cu(111) using the total-reflection high-energy positron diffraction (TRHEPD) technique [2].

TRHEPD is best suited for structure determinations of two-dimensional atomic sheets suspended on a substrate. Since the positron has a positive charge, opposite to the electron, the crystal potential acts as a potential barrier. When the positron beam is incident on the surface at a low glancing angle, total reflection occurs. The penetration depth of the positron beam under the total reflection condition corresponds to about the thickness of one atomic layer. On incidence with a glancing angle slightly beyond the critical angle of total reflection, the positron beam reaches the layer immediately beneath the topmost layer. Thus, TRHEPD is a surface-sensitive tool owing to the positive charge of positrons. TRHEPD apparatus using a linac-based intense positron beam has been constructed at the Slow Positron Facility, through collaboration between JAEA and KEK. It has already been used to reveal the structure of silicene on an Ag(111) substrate [3].

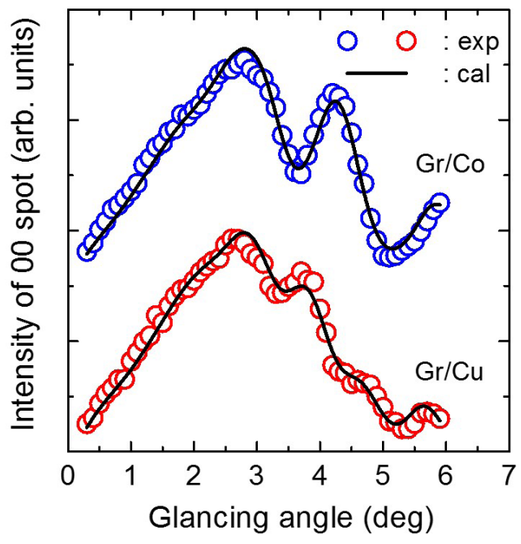

Figure 1: TRHEPD rocking curves of 00 (specular) spots for graphene on (upper part) Co(0001) and (lower part) Cu(111) substrates. Circles indicate experiments and lines are curves calculated using the optimum values.

The TRHEPD rocking curves (diffracted intensity vs glancing angle) observed for graphene on Co(0001) and Cu(111) substrates represent different shapes, depending on the substrate material (**Fig. 1**). From analysis based on dynamical diffraction theory, the spacing for the Co substrate was determined to be 2.06 Å, which is much smaller than the layer distance in solid graphite. In the case of the Cu substrate, the spacing was found to be 3.34 Å, which is nearly the same as the layer distance in graphite. Therefore, the results indicate that the interaction with the Co(0001) substrate is much greater than that for the Cu case. No buckling was observed in the graphene for both substrates.

The value of the spacing determined for the Co substrate is in good agreement with the theoretical prediction [1]. The value for the Cu substrate is between the results of density functional theory (DFT) calculations [1] and van der Waals DFT calculations [4]. As pointed out in the previous theoretical study [1], the spacing between the graphene and the substrate is closely related to the hybridization with *d*-states of the substrate material.

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