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Spacing between graphene and metal substrates studied with total-reflection high-energy positron diffraction

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ABSTRACT

The spacing between graphene and metal substrates has been investigated using total-reflection high-energy positron diffraction (TRHEPD). The rocking curve analysis performed, based on the dynamical diffraction theory, shows that the spacing between the graphene layer and a substrate of Cu(111) and that between graphene and a Co(0001) substrate are 3.34 Å and 2.06 Å, respectively. The former is close to the interlayer spacing in graphite, suggesting a weak interaction with the substrate material, whereas the latter value experimentally verifies that, in the case of graphene on Co(0001), there is a strong interaction with the substrate.

1. Introduction

Graphene has been attracting increasing attention since the report of its isolation, with focus on its features such as high carrier mobility, high thermal conductivity and robust mechanical property [1]. Due to the weak spin–orbit interaction, graphene has a large spin diffusion length, and so is a good candidate for potential applications in spintronic devices [2].

Theoretical calculations demonstrate that the nature of the interaction with a metal substrate depends on the actual substrate material and, furthermore, that this modulates the shape of the energy dispersion of the so-called Dirac cone for a freestanding graphene [3]. In addition, the theoretical studies have shown that the spacing between the graphene and the substrate can be classified into two groups, depending on the interaction between them: weak interaction with noble metal substrates; and strong interaction with transition metal substrates [3,4]. Furthermore, the theoretical calculations for graphene/metal systems involve the added complexity of incorporating the influence of a long-range van der Waals interaction, which still remains a challenging issue [5]. Thus, experimental determination of the spacing between graphene and the substrate is crucial to elucidate the origin of the electronic property of graphene adsorbed on the particular substrate.

In this study, we determine the spacing between the graphene and the metal substrates of Cu(111) and Co(0001), using total-reflection high-energy positron diffraction (TRHEPD).

Although the spacing between graphene and metal substrates has been extensively investigated from a theoretical basis, reports on the experimental determination of this property are limited [4], with the spacing for graphene/Cu(111) yet to be confirmed experimentally. For graphene/Co(0001), a scanning tunneling microscopy study has shown that the spacing is in the range 1.5–2.2 Å [6].

The positive charge of the positron allows TRHEPD to be used as a surface-sensitive tool [7–9], ideal for a detailed analysis of surface and near-surface layers; a positron beam incident upon a crystal at a grazing angle can undergo total reflection at the surface. The penetration depth of the positron under the total reflection condition is less than approximately 2 Å, which corresponds to the thickness of one atomic layer. When the glancing angle is slightly over the critical angle for total reflection, the positron beam reaches the layer just below the topmost layer. Thus, TRHEPD is a technique suitable for determining the atomic configuration of graphene adsorbed onto a substrate.

2. Experimental procedure

Experiments were carried out at the Slow Positron Facility, KEK,

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Japan. An intense positron beam was produced from pair creation via bremsstrahlung radiation in a Ta convertor using a dedicated 55-MeV electron linac and moderated with a W foil assembly [10]. The brightness of the positron beam was then enhanced using a transmission type remoderator comprising of a 100-nm W film. The resulting high-brightness monoenergetic positron beam was accelerated to 10 keV. The glancing angle (θ) of the incident positron beam was varied by rotating the sample incrementally in steps of 0.1°, and the resultant diffraction patterns were observed using a microchannel plate with a phosphor screen and a CCD camera. Rocking curves of the 00 (specular) spots, i.e. the 00 spot intensity versus θ, were then extracted from the measurements, which were conducted at room temperature. Details of the experimental setup are described elsewhere [11].

The samples studied were produced in the following way. A crystalline Cu(111) thin film, of thickness 500 nm, was grown on a α-Al_2O_3(0001) substrate by the deposition of Cu atoms at room temperature, followed by annealing up to 1270 K in a H_2 atmosphere. Graphene with a single layer was grown on the film by exposing the Cu film to a gas mixture (Ar, H_2, CH_4) at 1270 K in an electric furnace [12,13]. A crystalline Co(0001) thin film, with a thickness of 20 nm, was grown on the α-Al_2O_3(0001) substrate by the deposition of Co atoms at 620 K. Then, single layer graphene was grown on the film by an exposure to acetylene at 870 K [14–16]. The formation of single layer graphene on the Cu(111) and on the Co(0001) substrates was confirmed using Raman spectroscopy and x-ray photoelectron spectroscopy, respectively [12,14]. The flat and uniform graphene on these substrates was also confirmed using atomic force microscopy and reflection high-energy electron diffraction. Fig. 1 shows schematic drawings of graphene on the surface of the metal substrate.

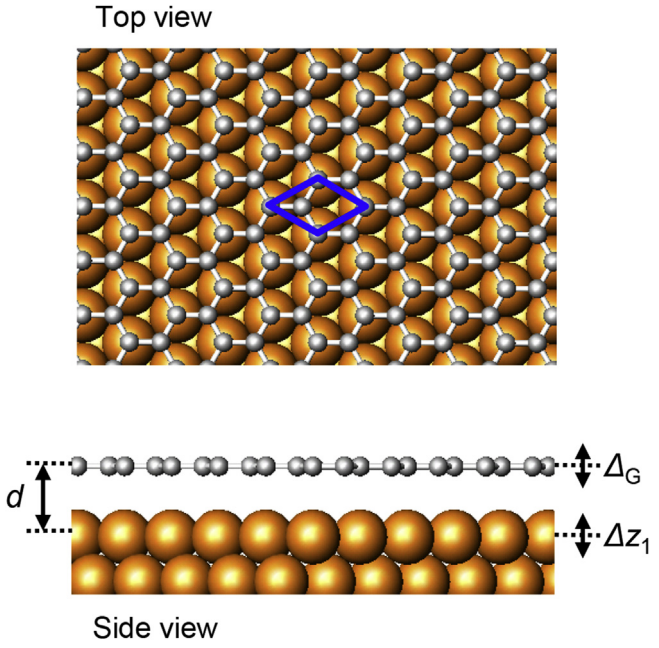

Fig. 1. Schematic drawings of graphene on a metal substrate. Gray circles indicate the C atoms. Orange circles are the Cu or Co atoms. The spacing between the bottom of graphene and the first Cu or Co layers is denoted by *d*. The magnitude of the buckling for the graphene and the shift of the top Cu or Co layer from the bulk position are denoted by Δ_G and Δ_{z1}, respectively. The rhombus indicates the unit cell of graphene. (A colour version of this figure can be viewed online.)

3. Results and discussion

Fig. 2a and b shows the TRHEPD rocking curves of 00 spots derived for single layer graphene on the Cu(111) and Co(0001) surfaces. The incident azimuths correspond to 13° off the [11$\bar{2}$] direction for the graphene/Cu(111) and 15° off the [1$\bar{1}$00] direction for the graphene/Co(0001) – known as the one-beam condition [17]. The intensity of the 00 spots under this condition depends only on the vertical components of the atomic positions and the number density of atoms in each layer. The critical angles for total reflection for graphene (mean inner potential, V_0, of 11.5 V [18]), Cu

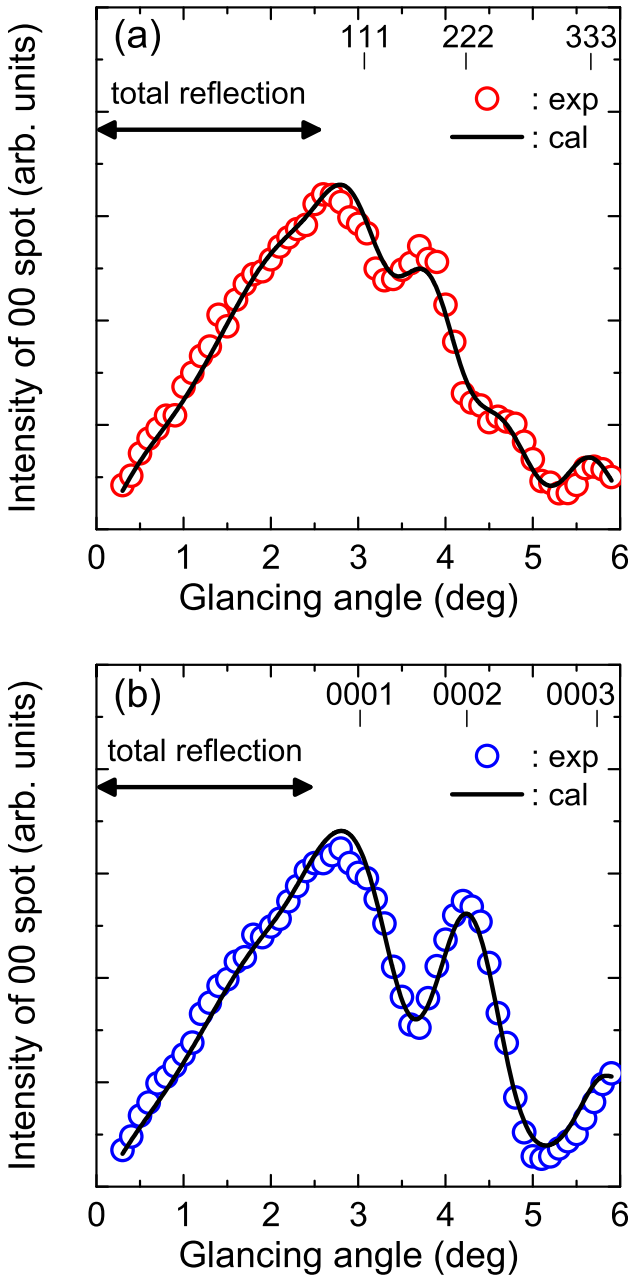

Fig. 2. TRHEPD rocking curves of 00 spots for graphene (a) on Cu(111) and (b) on Co(0001) substrates. Open circles and solid lines indicate the experimental and calculated values, respectively. The total reflection regions for (a) Cu and (b) Co crystals are shown by double-headed arrows. The indices of Bragg reflections for (a) Cu(111) and (b) Co(0001) are shown at the top of figures. (A colour version of this figure can be viewed online.)