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PEEM observation of band alignment on graphene/hexagonal boron nitride laminate structure

Since high-temperature high-pressure (HTHP) synthesized hexagonal boron nitride (h-BN) has high-quality crystallinity, usage for the substrate of high-speed graphene FET is being studied. It is important to clarify the band alignments for further applications of h-BN/Graphene substrates. Photoelectron spectroscopy is a powerful tool to determine the band offset at material interfaces. To evaluate the band offset at a conventional metal/insulating film interface with ordinary photoelectron spectroscopy, laminated samples with a size of several millimeters need to be prepared. However, the peeled h-BN single crystal has a small size of several tens of μm, so it is difficult to measure the band offset of an graphene/h-BN laminated sample using conventional photoelectron spectroscopy. In this study, photoemission electron microscopy (PEEM) is used to determine the band offset of a laminated structure of HPHT h-BN and graphene. Valence band photoelectron spectra are collected by micro ultraviolet photoelectron spectroscopy (UPS) using a PEEM equipped with an electron energy analyzer, which allowed the band alignment of h-BN and the graphene/h-BN laminated structure to be obtained[1].

The h-BN crystal synthesized by HTHP method was peeled off with a tape and transferred onto a Si substrate to give single-crystal h-BN on the Si substrate. The graphene film grown by the thermal CVD on the Cu foil was transferred onto the h-BN/Si substrate. The photoelectron microscopy and spectroscopy measurements were carried out using the PEEM equipment (IS-PEEM, FOCUS GmbH, Germany) equipped with a commercially available analyzer[2,3]. He I resonance line (21.22 eV) was used as the excitation light source in photoemission experiments.

The PEEM image and photoelectron spectra of CVD graphene on HTHP h-BN are shown in the Figure 1. In area (1), the σ peak derived from h-BN was clearly observed, so it was found that graphene was broken and the underlying h-BN was exposed. On the other hand, area (2) was covered with graphene, so that the intensity of the σ peak was weakened. We have determined the band alignment of the HTHP h-BN/graphene structure from these peak positions and secondary electron spectra.
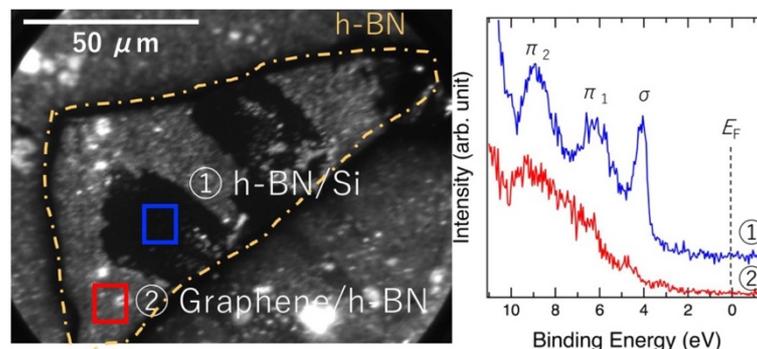
Figure 1: PEEM image of h-BN/graphene and its photoelectron spectra. The dash-dot line surrounded the outline of bulk h-BN and the darker area indicates the break of graphene.

The band diagram of h-BN is shown in Fig. 2 (a). The kinetic energy at the position corresponding to the conduction band minimum (CBM) is 23.65 eV. Because the band gap of h-BN is 5.97 eV, the valence band maximum (VBM) exists below 5.97 eV from CBM. The Fermi level position is supposed to be 4.0 eV upper from the σ peak position[4]. The Fermi level is present at 0.87 eV from the VBM. However, this is a band structure of the detection depth range of ultraviolet photoelectron spectroscopy (approximately 1 nm from the surface). It should be noted that it may be different from the position of the Fermi level in the deeper bulk.

Next, the band diagram of the graphene/h-BN laminate was determined. From the valence band spectra of graphene/h-BN substrate in Fig. 1, it is found that the photoelectron intensity gradually increased with binding energy. In addition, although the intensity of the σ peak was attenuated when h-BN was covered with graphene, the σ peak derived from the h-BN substrate was observed in area (2) in Fig. 1. Because both surfaces were covered with conductive graphene, the spectral shift caused by charge up can be neglected. Therefore, Fermi level of these spectra was obtained from the Au film deposited on the sample holder. Nevertheless, the σ peak position of graphene-covered h-BN was E_B = 4.85 eV in Fig.1, which was shifted to higher binding energy compared with that of the uncovered h-BN substrate. This result indicates that Fermi level of h-BN moved to the center of the band gap upon coating with graphene, as shown in Fig. 2 (b). The work function of graphene on h-BN was 4.40 eV. Because work function of pristine graphene is 4.5 eV [5], the graphene sample in this work shows weak n-type conductivity.

As described above, the band offsets of h-BN and graphene/h-BN laminates can be obtained from PEEM and UPS observations. We believe that the change of Fermi level position of h-BN induced by forming a graphene/h-BN laminate structure will be important in future fabrication of two-dimensional electronic devices. However, the mechanism behind the change of EF of h-BN induced by graphene is still unknown; further research in the future is necessary. In presentation, the detail of spectral analysis will be demonstrated.
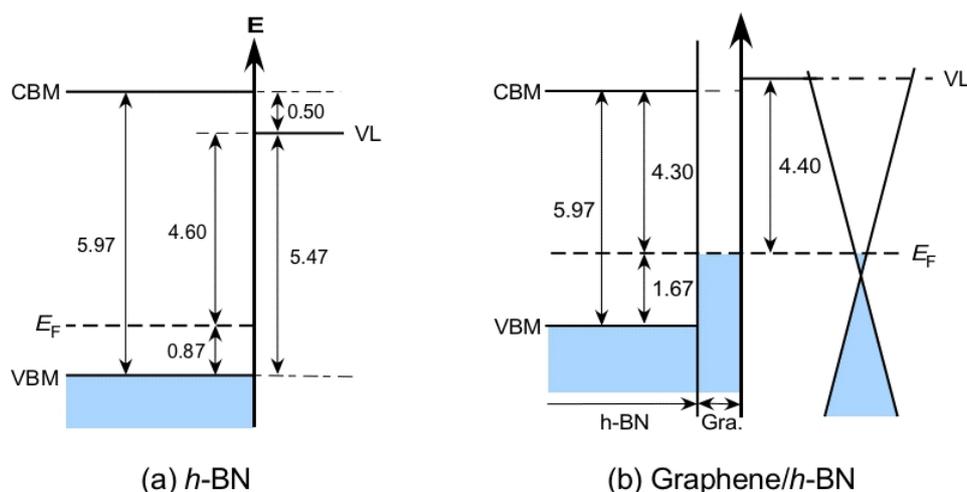
Figure 2: Band diagram of (a) h-BN and (b) graphene/h-BN laminate structure.

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