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Valence band evaluation of graphene using *in-situ* photoelectron spectroscopy with non-monochromatic He I line

The molecular adsorption on graphene causes the modulation of conductivity of graphene, so that the application of graphene for gas sensors are expected. To evaluate the conductivity type of graphene by photoelectron spectroscopy (PES), the angle-resolved PES is widely used because it can directly observe the Dirac-corn. However, ARPES measurements have been performed usually in synchrotron facility [1] or using monochromatic ultraviolet light such as He I [2] or He II resonance lines. In addition, ARPES needs a long measurement time, so that the changes of valence band during heating or adsorption cannot be followed. In this study, we try to evaluate the valence band of graphene using "angle-integrated PES" with non-monochromatic He I line in order to evaluate the changes of conductivity of graphene during the adsorption and/or desorption of molecules.

The experiments were performed UPS apparatus[3] equipped with an infrared heating (GVH298, THERMO RIKO Co., Ltd). Samples can be heated without generation of the electric and magnetic fields, so that spectra at the high temperature can be measured without any modification of the kinetic energy and intensity. Graphene was grown on Cu foils by CVD, and then transferred graphene on a SiO_2/Si substrate.

Generally, non-monochromatic He I resonance line is unsuitable for the evaluation of valence band of graphene because the He I line contains not only the strongest He Iα line (21.22 eV) but also He Iβ (23.08 eV) and He Iγ (23.74 eV)lines. These Iβ and Iγ lines make the Dirac-corn and Fermi level of graphene fuzzy. To eliminate the effect of these high energy light, the removal filter using Fourier transform has been developed. Figure 1 (a) and (b) shows the comparison between spectra as measured and after filtering of the graphene/SiO_2 substrate. The filtered spectrum seems to shift holistically to high binding energy side, and the structure of valence band can be observed more clearly. It is found from the fitting analysis shown in Fig. 1(c) that the stepped spectrum indicates the Fermi level of graphene, of course the Fermi level completely agrees with that of metals. This result suggests that this graphene is n-type as shown in the inset of Fig. 1(c).

The temperature dependence of spectra using the filter is shown in Fig. 2. The intensity near the Fermi level increases with increasing temperature. This is because the position of Fermi level is changed by desorption of absorbed molecules on graphene such as H_2O and CO_2. In addition, the changes of Fermi level agrees with the result from XPS measurements at BL23SU, SPring-8.

In summary, we can measure the shift of Fermi level depending on the temperature by using removal filter based on Fourier transform. This shift is caused by desorption of absorbed molecules on graphene, and we can follow up the change because of using high-intensity non-monochromatic He I resonance line. In presentation, we will show the temperature dependence of chemical components of absorbed molecules.

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References

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Figures

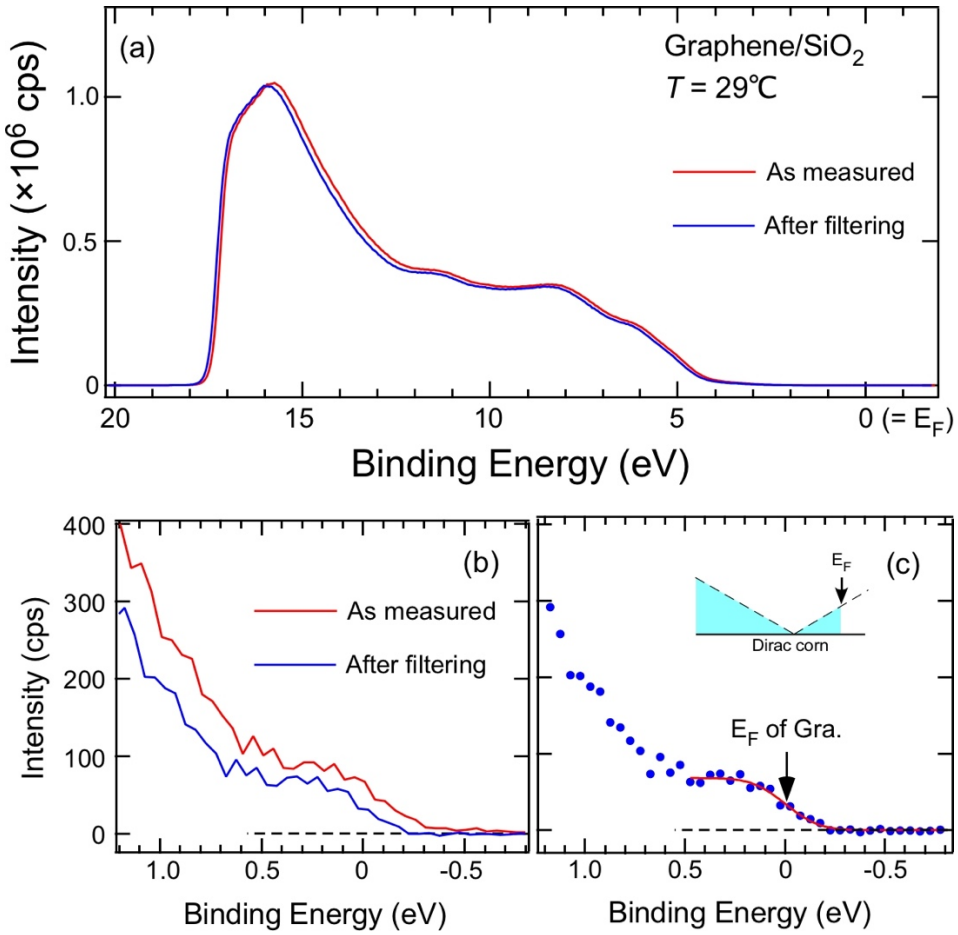

Figure 1: (a) Photoelectron spectra of graphene/SiO_2 substrates measured using non-monochromatic He I resonance line. The blue line is filtered spectrum in order to eliminate the effect of the high-energy light. (b) Magnification of spectra near the Fermi level. (c) Fitting analysis of spectrum using Fermi-Dirac function. The Fermi level of graphene agree completely with the that of metals.

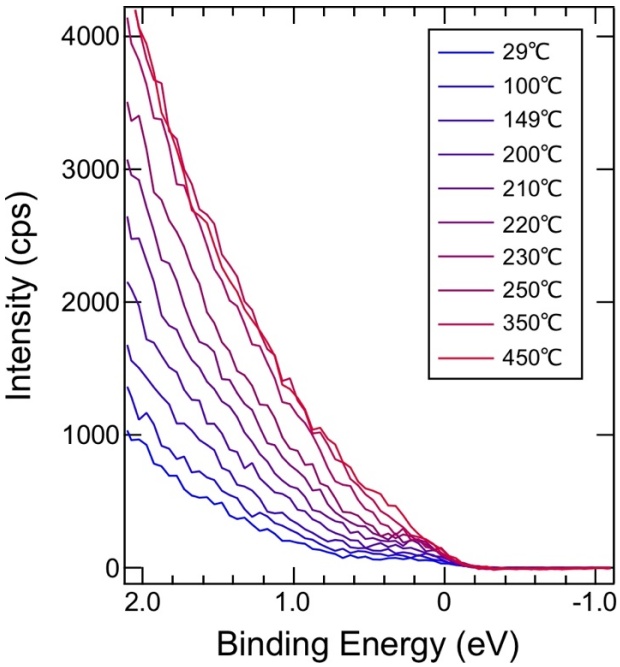

Figure 2: Temperature dependence of spectra near the Fermi-level. The intensity of Fermi-level increases with temperature.