Angle-resolved photoemission spectroscopy study on graphene using circularly polarized light

Angle-resolved photoemission spectroscopy study on graphene using circularly polarized light

Choongyu Hwang

Department of Physics, Pusan National University, Busan 609–735, Korea

E-mail: ckhwang@pusan.ac.kr

Abstract

We have investigated graphene using circularly polarized light via angle-resolved photoemission spectroscopy. We observe that photoelectron intensity rotates around a constant energy contour towards the opposite direction upon changing the chirality of light. Interestingly, the circular dichroism is found to be asymmetric with respect to the Dirac energy, which is not explained by the Berry phase effect (Liu *et al* 2011 *Phys. Rev. Lett.* **107** 166803). We also report that the energy spectra taken using the light with different chiralities show a finite separation from each other. We discuss possible origins of the unusual circular dichroism observed in graphene.

Keywords: graphene, circular dichroism, angle-resolved photoemission spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

The interaction of light with a quasiparticle can reveal fundamental information on the quasiparticle. For example, the light-electron interactions in graphene provide a direct measurement of quantum phases of electrons such as the Berry phase [1] and the sign of hopping integrals within the tight-binding formalism [1, 2], and the light-spin interactions in a topological insulator provide a capability of manipulating spin polarization [3] when linearly polarized light (LP) is used for both cases. These recent studies were performed through the comparison between experimental results and the calculated photoemission matrix elements within the tight-binding formalism [1, 3].

Circularly polarized lights have also been used to understand the photoemission matrix element in graphene [4, 5], while they are well-known sources to probe angular momentum-related phenomena such as spin–orbit coupling [6], chirality [7], and exchange splitting [8]. For graphene, the circularly polarized light gives rise to asymmetric photoelectron intensity with respect to a high symmetry direction at constant energies [4, 5], of which asymmetry is reversed upon changing the chirality of light. Such circular dichroism

has been attributed to either Berry phase of graphene [4] or final states [5].

In this report, we show that the photoelectron intensity from graphene exhibits circular dichroism consistent with previous experimental results [4, 5]. However, we found that the circular dichroism shows unusual dependence on the electron binding energy, which is not described by the Berry phase effect [4]. We also report that the energy spectra taken using light with different chiralities show a slight deviation from each other, suggesting that the final state effect might not be the only origin of the circular dichroism [5]. We discuss possible origins of the unusual circular dichroism observed in graphene.

2. Experimental details

Single-layer graphene samples were grown epitaxially on n-doped $6H$-SiC(0001) surfaces using the electron-beam heating method [11]. An SiC sample was mounted in a prep-chamber with a base pressure of 5×10^{-10} Torr to remove a thick oxide layer from the sample by heating up to 600 °C for a few hours. The clean sample was heated to 1000 °C under Si flux and then flashed at 1400 °C to finally grow
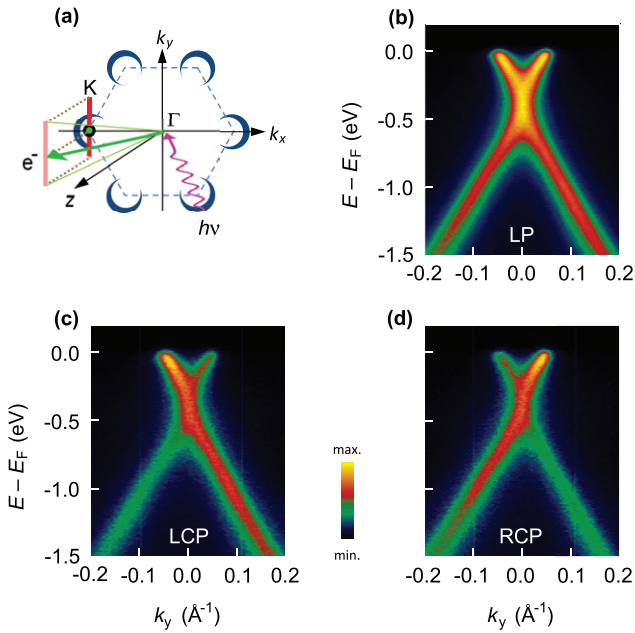
Figure 1. (*a*) An experimental geometry for ARPES measurement. A beam of monochromatic lights with energy $\hbar\omega = 50$ eV is incident on a sample. (*b*) Measured intensity map of graphene using linearly polarized light (LP). (*c*)–(*d*) Measured intensity maps of graphene using left (LCP: panel (*c*)) and right (RCP: panel (*d*)) circularly polarized lights.

graphene. Polarization-dependent angle-resolved photoemission spectroscopy (ARPES) experiments were performed, for thus prepared graphene sample, at 15 K at the beamline 12.0.1 of Advanced Light Source at the Lawrence Berkeley National Laboratory. Photon energy was set to be 50 eV. For the same geometry, we have changed the light polarization from LP to left and right circular polarizations, LCP and RCP, respectively.

3. Result

Figure 1(*a*) shows the typical geometry for the ARPES measurements, where a beam of monochromatized light with energy $h\nu$ is incident on a sample. For a single measurement, the photoelectron intensity along the red line shown in figure 1(*a*) is obtained simultaneously, so that the intensity of left and right branches of the conical dispersion of graphene can be directly compared. Single-layer nature was confirmed by the ARPES map taken using LP perpendicular to the ΓK direction as shown in figure 1(*b*). Single conical dispersion is observed with the Dirac energy, E_D, lying ∼0.4 eV below the Fermi energy, E_F, due to the intrinsic electron-doping by the substrate [12]. The left and right branches of the conical dispersion show almost symmetric intensity, except a lower $E − E_F$, which is likely due to imperfect linear polarization, e.g. a finite contribution of perpendicular polarization which can slightly rotate photoelectron intensity in the k_x–k_y plane [1]. On the other hand, while the experimental geometry remains

the same, significant asymmetry is observed upon changing light polarization from LP to LCP as shown in figure 1(*c*). Photoelectron intensity of the right branch is significantly suppressed above E_D, whereas the other side shows suppressed spectral intensity below E_D. This asymmetric intensity is reversed upon changing light polarization from LCP to RCP as shown in figure 1(*d*), resulting in circular dichroism in photoelectron intensity.

To further investigate this dichroic effect, we show constant energy maps in the k_x–k_y plane as a function of $E − E_F$ for LCP and RCP in figures 2(*a*) and (*b*), respectively. Photoelectron intensity around a constant energy contour shows intensity variation along the specific direction in the momentum space, similar to the previous experimental results taken using LP [1, 2, 4, 13, 14]. However, the difference of the result using LCP from the one for LP is a slight rotation of the intensity along the counter-clock-wise direction with respect to $k_y = 0$, that is reversed towards the clock-wise direction for RCP. This circular dichroism is consistent with previous experimental results [4, 5].

The rotation of intensity is better visualized via an intensity profile around the constant energy contour. In figure 3(*a*), at $E − E_F = 0$, the intensity profile for LCP shows its maximum (denoted by the black arrow) at $\theta \sim \pi/18$, when θ is the rotational angle with respect to $k_y = 0$. Meanwhile, as $E − E_F$ decreases below E_D, the intensity maximum is shifted towards lower angles, which results in asymmetric rotation with respect to E_D (for example, compare 0.0 eV versus −0.8 eV and −0.2 eV versus −0.6 eV spectra, denoted by arrows). With further decreasing $E − E_F$, e.g. at −1.0 eV, another spectral weight at a positive angle appears as denoted by the gray line. This becomes clear when the intensity profile is fitted with two Gaussian peak functions as shown in figure 3(*c*), where blue-dotted lines are Gaussian peaks and the red-dotted line is the fit to the experimental data. Upon changing the light polarization to RCP, the rotational angle is flipped with respect to $\theta = 0$, while the observed spectral features, i.e. asymmetric rotational angle with respect to E_D and additional spectral weight at the opposite direction, remain consistent. The position of intensity maxima for LCP and RCP is summarized in figure 3(*d*) with red and blue symbols, respectively. As a result, we find that the circular dichroism, i.e. the difference in rotational angle, is highly asymmetric with respect to E_D.

4. Discussion

Possible explanations of the asymmetric circular dichroism include an experimental artifact such as the finite contribution from double-layer graphene, many-body effects, the Berry phase effect [4], the final state effect [5], and angular-momentum related phenomena [6–8]. The contribution from double-layer graphene is unlikely to be the origin of the asymmetry, because the rotational angle of double-layer
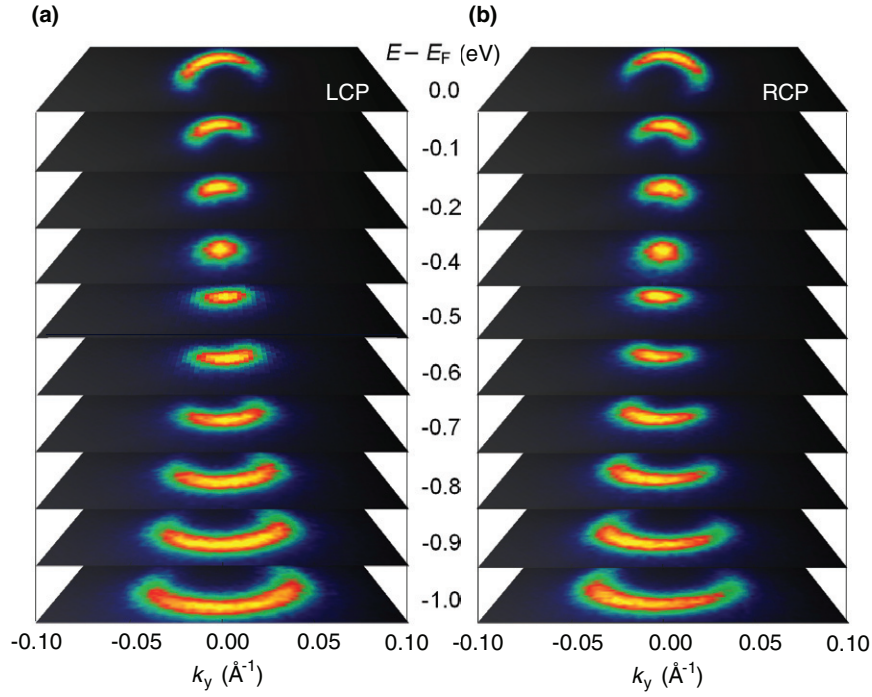
Figure 2. (*a*) and (*b*) Constant energy maps at several different energies taken using LCP (panel (*a*)) and RCP (panel (*b*)).
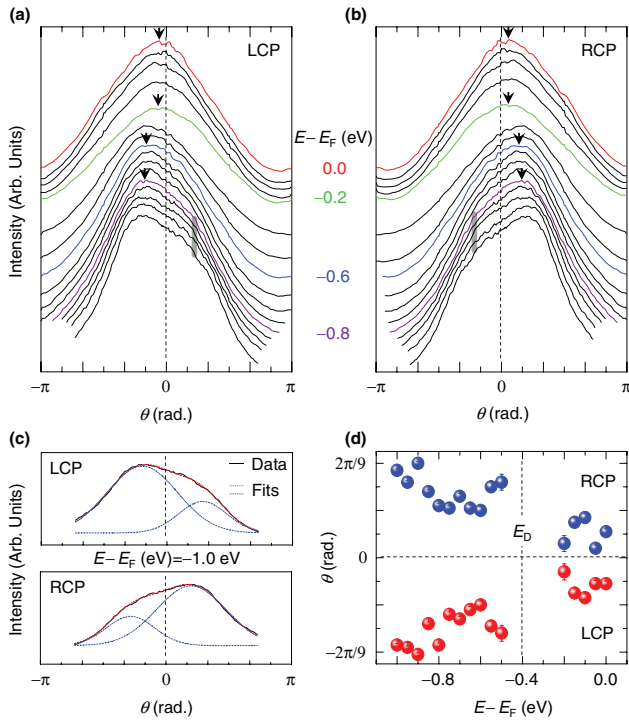

Figure 3. (*a*) and (*b*) The intensity profiles for LCP (panel (*a*)) and RCP (panel (*b*)) as a function of rotational angle with respect to the intensity maxima for LP. The intensity was integrated over the finite radius, e.g. $\Delta r \sim 0.03$ Å^{-1}. The black arrows indicate the intensity maximum and the gray bar indicates an additional spectral weight in intensity profile which appeared at lower $E - E_F$. (*c*) The intensity profile of the data in panels (*a*) and (*b*) at $E - E_F = -1.0$ eV. Experimental data, the Gaussian peak function, and the fit curve to the experimental data are shown in black-solid, blue-dotted, and red-dotted lines, respectively. (*d*) The angle of intensity maximum for LCP (red symbols) and RCP (blue symbols) as a function of $E - E_F$.

graphene is still expected to be symmetric with respect to E_D. The epitaxial graphene on an SiC(0001) substrate is intrinsically electron-doped [12], which results in asymmetric electron self-energy with respect to the Dirac energy due to the many-body interactions [9, 10]. This might indicate that the asymmetric photoelectron intensity might be related to the many-body effects. However, within our knowledge, it is not clear how the typical many-body effects (such as electron-electron and electron-phonon interactions) are related with the circularly polarized lights. A previous study has claimed that the Berry phase of charge carriers in graphene is associated with the circular dichroism [4]. However, the Berry phase should result in a symmetric dichroic effect with respect to E_D, because the electron band structure of graphene is symmetric with respect to E_D. This is different from our results taken as a function of $E - E_F$ (figures 2 and 3), hence making the Berry phase scenario less likely as the origin. Another measurement in conjunction with the first principles calculations reported that the circular dichroism is related with the final state effect, by showing that the dichroism is changing upon varying photon energy [5]. In other words, the calculations predict that higher (lower) photon energy results in a smaller (bigger) dichroic effect [5]. This can be interpreted that lower (higher) $E - E_F$ may result in a bigger (smaller) dichroic effect in the ARPES map taken using a single photon energy, which is qualitatively similar to the observed dichroic effect in figures 2 and 3.

To further investigate the asymmetric circular dichroism, in figure 4, we compare energy-momentum dispersions measured for the same sample at the same experimental geometry, but using two different light polarizations of LCP and RCP. The standard recipe, i.e. a fit with a Lorentzian
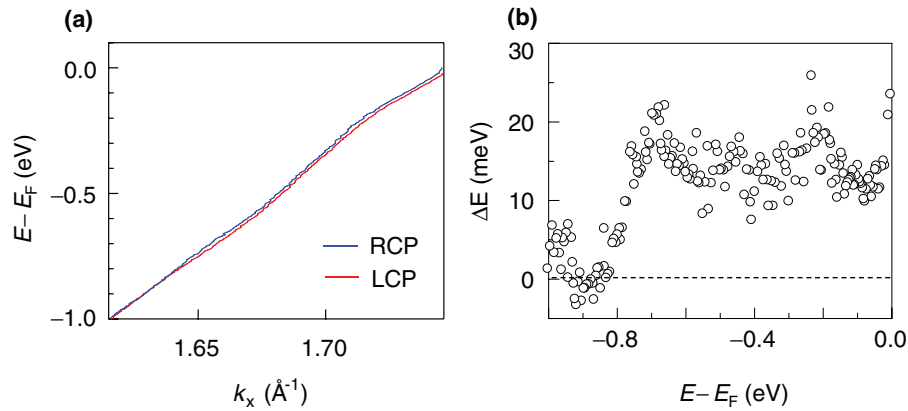
Figure 4. (*a*) The fitted energy-momentum dispersions for LCP (red curve) and RCP (blue curve). (*b*) The difference in energy of the dispersions shown in panel (*a*).

peak function for more than 1000 consecutive momentum distribution curves, is employed to extract energy momentum distributions shown in figure 4(*a*). Interestingly, two dispersions taken by LCP and RCP do not coincide perfectly with each other near E_F. As shown in figure 4(*b*), the average separation, ΔE, is ∼15 meV, which abruptly decreases below $E - E_F = -0.7$ eV and increases with further decreasing $E - E_F$. This observation might suggest that each chirality of the light is sensitive to two different energy spectrum separated by ΔE near E_F. This unusual behavior was not taken into account in the photon energy dependent dichroic effect within a single energy spectrum, i.e. the final state effect [5]. The experimental artifact, such as a slightly shifted photon beam upon changing the chirality of light (that can cause a similar effect), is easily excluded, because ΔE is not constant over the whole energy range, but changes as a function of $E - E_F$, whose origin is not clear.

In fact, circularly polarized lights have been widely used to probe spin or orbital angular momentum of quasiparticles [6–8]. Magnetic and heavy nuclei materials show circular dichroism, manifesting spin–orbit coupling [6], chirality [7], and the presence of polarized spins [8]. In graphene, the relativistic effect that entangles spin and pseudospin degrees of freedom is predicted to lift the spin degeneracy of the energy spectrum, via spin–orbit coupling [16]. However, intrinsic spin–orbit coupling is estimated to be less than 0.1 meV [16]. On the other hand, breaking up-down symmetry by a substrate can result in substantial extrinsic spin–orbit coupling, so-called Rashba-type spin–orbit splitting [17]. Hence, we speculate that the unusual circular dichroism observed in epitaxially grown graphene on an SiC(0001) might be related not only with the final state effect [5], but also with the spin–orbit coupling. Our result might be interesting when compared to graphene on an Au/ni(111) substrate showing the Rashba type spin–orbit coupling with an estimated split energy of 13 meV [18], because one of the plausible origins of the enhanced Rashba effect for graphene/Au/Ni is the presence of a high nuclear charge of the substrate [19], whereas graphene/SiC does not have high nuclear charges. The spin–orbit coupling in graphene on a substrate [17] is certainly an appealing scenario in terms of the future applications of graphene as a

key material for the fabrication of spintronic devices and for the realization of the ferromagnetic quantum Hall effect [20]. However, we emphasize that our results invite further experimental and theoretical investigations to understand the observed unusual circular dichroism in epitaxially grown graphene on the SiC substrate.

5. Summary

In this report, we have shown that epitaxial graphene grown on an SiC(0001) substrate exhibits unusual circular dichroism. The dichroic effect varies as a function of electron binding energy, which is not explained by the Berry phase effect. In addition, the energy spectra also show an unusual dichroic effect, suggesting that the final state effect might not be the only origin of the circular dichroism. While the origin of the dichroic effect needs further investigation with combined experimental and theoretical studies, we speculate that the spin–orbit coupling enhanced due to the presence of a substrate might play a finite role in observed asymmetric circular dichroism.

Acknowledgments

References

[1] Hwang C *et al* 2011 *Phys. Rev.* B **84** 125422
[2] Gierz I, Henk J, Höchst H, Ast C R and Kern K 2011 *Phys. Rev.* B **83** 121408
[3] Jozwiak C *et al* 2013 *Nature Phys.* **9** 293
[4] Liu Y, Bian G, Miller T and Chiang T-C 2011 *Phys. Rev. Lett.* **107** 166803
[5] Gierz I, Lindroos M, Höchst H, Ast C R and Kern K 2012 *Nano Lett.* **12** 3900

[6] Kuch W and Schneiger C M 2001 *Rep. Prog. Phys.* **64** 147
[7] Polcik M *et al* 2004 *Phys. Rev. Lett.* **92** 236103
[8] Mulazzi M *et al* 2006 *Phys. Rev.* B **74** 035118
[9] Park C-H *et al* 2007 *Phys. Rev. Lett.* **99** 086804
[10] Park C-H *et al* 2009 *Phys. Rev. Lett.* **102** 076803
[11] Rollings E *et al* 2006 *J. Phys. Chem. Solids* **67** 2172
[12] Sellyer T, Emtsev K V, Speck F, Gao K-Y and Ley L 2006 *Appl. Phys. Lett.* **88** 242103
[13] Shirley E L, Terminello L J, Santoni A and Himpsel F J 1995 *Phys. Rev.* B **51** 13614
[14] Mucha-Kruczyński M *et al* 2008 *Phys. Rev.* B **77** 195403
[15] Saito R, Dresselhaus G and Dresselhaus M S 2000 *Phys. Rev.* B **61** 2981
[16] Kane C L and Mele E J 2005 *Phys. Rev. Lett.* **95** 226801
[17] Rashba E I 2009 *Phys. Rev.* B **79** 161409
[18] Varykhalov A *et al* 2008 *Phys. Rev. Lett.* **101** 157601
[19] Rader O, Varykhalov A A and Sánchez-Barriga J 2009 *Phys. Rev. Lett.* **102** 057602
[20] Brey L, Fertig H A, Côté R and MacDonald A H 1995 *Phys. Rev. Lett.* **75** 2562