

# Interference of excitons and surface plasmons in the optical absorption spectra of monolayer and bilayer graphene

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By using spectroscopy ellipsometry, we investigated the optical absorption spectra of monolayer and bilayer graphene in the deep-ultraviolet region up to 6.42 eV as a function of temperature. The optical absorption spectra of monolayer and bilayer graphene can be fitted by two Breit-Wigner-Fano (BWF) spectral functions, in which each BWF is originated by the interference of discrete excitonic spectra and continuous surface plasmon spectra. Each BWF peak shows narrower linewidth and larger peak intensity with increasing temperature. The unusual temperature dependence of the BWF peaks is understood by a shorter lifetime of the surface plasmon at a higher temperature, which gives a smaller BWF asymmetric parameter. The optical absorption by the surface plasmon is usually observed only at the surface of the three-dimensional crystal or two-dimensional material. The contribution of the surface plasmon becomes relatively larger in the case of monolayer or bilayer graphene than that of single-crystal graphite because of the two-dimensional nature of electrons. The observed optical absorption spectra are confirmed by calculating the complex dielectric function using the first-principles calculations.

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## I. INTRODUCTION

In two-dimensional (2D) materials, optical absorption occurs not only through single-particle excitation that includes excitonic excitation but also through collective excitation of electrons, a phenomenon known as surface plasmon polariton [1–5]. Because the bulk plasmon in three-dimensional materials exhibits a longitudinal wave, the bulk plasmon is not excited by a transverse wave of a photon. However, a plasmon at the surface of a material can be excited by light and propagates in the direction parallel to the surface which is known as a surface plasmon. A surface plasmon resonance is commonly used to observe nanoparticles on the metal surface, when the resonance condition for the surface plasmon is satisfied [6]. However, evaluating contributions of a surface plasmon and single-particle excitation in the optical absorption spectra is not well established because the surface plasmon frequency exists not in the visible (or infrared) light region but in the deep-ultraviolet (UV) or terahertz (THz) region, which corresponds to interband or intraband plasmons, respectively [6]. In our previous study, we observed the interference phenomena in the optical absorption of single-crystal graphite in the deep-UV region at 4–6 eV [7]. However, we did not discuss the contribution of a surface plasmon in the optical absorption of single-crystal graphite because we could not calculate the optical response at the surface of graphite by the first-principles

calculations. Since the surface plasmon phenomenon occurs less than 10 nm away from the surface, the contribution of a surface plasmon to optical absorption is expected to be relatively large in 2D materials. Furthermore, we can calculate the optical response of 2D materials, which includes the effect of surface plasmon by first-principles calculations. In this work, we investigated the optical absorption up to 6.42 eV for monolayer and bilayer graphene by spectroscopic ellipsometry. We found that the optical absorption peaks become larger and narrower with increasing temperature from 4.5 to 500 K. This unusual behavior is discussed by the temperature-dependent interference effect combined with the first-principles calculations of the complex dielectric function.

Monolayer graphene has attracted considerable attention from condensed matter physicists, chemists, semiconductor device engineers, and materials scientists since 2004 [8–11]. Graphene exhibits unusual many-body physics behavior, including strong electron-electron interactions [12] as well as quantum phase transitions and novel admixtures of these states because of 2D confinement of electrons [13]. Furthermore, graphene has several practical applications, such as in nanoelectronics, optoelectronics, photonics, and information processing, in which the surface plasmon has an important role [14–18]. Bilayer graphene has been recognized as a new material independent of monolayer graphene since 2018. The electronic properties of twisted bilayer graphene are strongly affected by the twist angle, indicating that the electronic band structure is modulated by angle-dependent interlayer interaction. These tunable electronic bands are exceptional because

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they can host various correlated electronic phases [19–22]. Thus, bilayer graphene has opened new avenues for developing high-performance twistrionic devices [23,24].

A systematic study of the optical properties of monolayer and bilayer graphene is essential to fabricate optoelectronics, photonics, and twistrionic devices for practical applications. Having knowledge of the temperature-dependent optical properties of a device is crucial to investigate the effect of self-heating on device performance. Furthermore, understanding the frequency-dependent optical properties is essential for improving the quality of materials and the efficiency and applicability of devices. Previous studies have reported that monolayer graphene exhibits intraband Drude conductivity in the THz to far-infrared frequency range and interband universal conductivity in the mid- and near-infrared frequency range [25–28]. Although many similar observations have been reported thus far, conflicting results have been obtained. Zou *et al.* [29] analyzed the temperature-dependent THz conductivity of bilayer graphene on the quartz substrate. They observed a strong peak at 2.7 THz, which was attributed to the enhancement of the density of states caused by the twisting of the bilayer graphene. Yang *et al.* [30] presented the first-principles calculations of many-body effects on the optical response of monolayer and bilayer graphene. They determined that infrared absorbance per graphene layer becomes approximately constant, whereas the exciton peak appears at 4.5 eV in monolayer and bilayer graphene. Kravets *et al.* [31] examined the spectroscopic ellipsometric spectra of monolayer graphene on a quartz substrate at room temperature. They observed a pronounced asymmetric peak at 4.6 eV, which was associated with a van Hove singularity in the density of states and excitonic effects of graphene. Wurstbauer *et al.* [32] employed image ellipsometry in the visible frequency range and determined that the optical constants of monolayer graphene were dependent on the SiO<sub>2</sub> and GaAs substrates. Chae *et al.* [33] reported the absorbance spectra of freestanding monolayer and bilayer graphene at room temperature. They observed an asymmetric absorption peak at 4.7 eV, which was attributed to an excitonic resonance. Santoso *et al.* [34] presented the optical conductivity spectra of monolayer and bilayer graphene on SiC substrates at room temperature. They noted that monolayer and bilayer graphene exhibited marked excitation at 5.4 eV, which was a mixture of interband transitions from  $\pi$  to  $\pi^*$  at the  $M$  point and a  $\pi$  plasmonic excitation, and a resonant exciton at 6.3 eV. Li *et al.* [35] and Fang *et al.* [36] have determined the spectroscopic ellipsometric spectra of monolayer and bilayer graphene on the fused silica and sapphire substrates at room temperature. They determined that monolayer and bilayer graphene exhibited a strong absorption peak at 4.8 eV and an additional weak absorption peak at 6.4 eV. These two absorption peaks were attributed to the resonant excitons at the  $M$  and  $\Gamma$  points of the Brillouin zone, respectively. El-Sayed *et al.* [37] investigated the effects of SiO<sub>2</sub>, quartz, and glass substrates on the optical constants of monolayer graphene through spectroscopic ellipsometry. They observed that the difference in the optical constants of monolayer graphene on the three substrates did not exceed 5%. Wu *et al.* [38] examined the temperature-dependent optical properties of monolayer and bilayer graphene on Si and SiO<sub>2</sub>/Si

substrates through spectroscopic ellipsometry. They reported that monolayer and bilayer graphene exhibited marked absorption in the UV region. When the temperature was increased from 300 to 500 K, the refractive index of monolayer graphene on the Si substrate gradually increased and its extinction coefficient decreased. In addition, Igarashi *et al.* [39], Yanagi *et al.* [40], and Satco *et al.* [41] have observed intersubband plasmon optical absorption in electrochemically doped carbon nanotube films. Sasaki *et al.* [42] indicated that the interband plasmon was expressed by the azimuthal transverse magnetic mode. Satco *et al.* [43] calculated the optical absorption spectra as a function of  $(n, m)$  of a carbon nanotube and Fermi energy to examine the intersubband plasmon excitation.

Most optical studies have conducted measurements at room temperature and narrow frequency ranges. However, the lifetime of a plasmon is shorter than that of an electron photoexcited by single-particle excitation, and the lifetime depends on temperature. In this study, we examined the temperature-dependent optical properties of monolayer and bilayer graphene at 4.5–500 K within the spectral range of 0.73–6.42 eV through spectroscopy ellipsometry. The wide temperature and spectral ranges enabled us to characterize the dispersion of the complex refractive index, complex dielectric function, and optical absorption coefficient. Furthermore, we compared our experimental results with the calculated complex dielectric function by using the first-principles calculations. The goal of this study is to uncover anomalous deep-UV electronic excitation in monolayer and bilayer graphene and to verify many-body interactions. The findings of this study can serve as a valuable reference for quantitatively investigating the effect of temperature- and frequency-dependent electromagnetic response on the performance of graphene-based optoelectronics, photonics, and twistrionic devices.

## II. METHOD

### A. Experiments

Monolayer and bilayer graphene samples were grown on Cu and Cu-Ni alloy thin films by using the chemical vapor deposition (CVD) method [44–47]. The catalyst films were deposited on  $c$ -plane sapphire, and graphene was grown by ambient pressure CVD at 1075°C and 1085°C for the monolayer and bilayer graphene, respectively. The CVD time for bilayer graphene was 6 hours to make Bernal stacking [47]. After growth, graphene was transferred to a sapphire or SiO<sub>2</sub>/Si substrate by etching the catalyst film in an aqueous ammonium persulfate solution while protecting graphene with a polymethylmethacrylate (PMMA) thin film, followed by removal of PMMA with acetone. The monolayer and bilayer graphene samples were verified through atomic force microscopy and Raman spectroscopy [44–47]. Spectroscopic ellipsometer measurements were performed at room temperature in the spectral range of 0.73–6.42 eV at the incident angles of 55°, 60°, 65°, 70°, and 75° on an M-2000U ellipsometer from J. A. Woollam Co.

We adopted the stacked layer model, including a sapphire substrate, thin film, and surface roughness as well as

TABLE I. Fitted parameters of the stacked layer model for the ellipsometric spectra of monolayer and bilayer graphene.

Layer	Monolayer	Bilayer
Surface roughness (nm)	$0.03 \pm 0.01$	$0.06 \pm 0.01$
Film thickness (nm)	$0.36 \pm 0.07$	$0.67 \pm 0.13$
Sapphire substrate (mm)	0.5	0.5

an air ambient structure, to fit raw ellipsometric parameters of  $\Psi$  and  $\Delta$  [48]. The fitting parameters of the model are listed in Table I. Through spectroscopic ellipsometry, we determined that the thicknesses of monolayer and bilayer graphene are  $0.36 \pm 0.07$  and  $0.67 \pm 0.13$  nm, respectively; these values are similar to those reported in the literature [44–47]. The independently measured ellipsometric spectra at different incident angles and the modeled curves are in good agreement, as presented in Supplemental Material Fig. 1 [48]. For temperature-dependent ellipsometry measurements at 4.5–500 K, the sample was mounted in a Janis ST-400 continuous-flow liquid helium cryostat. Then ultrahigh vacuum was applied at a base pressure of  $10^{-8}$  Torr at an incident angle of  $70^\circ$  [49–51].

### B. Theoretical model

Electronic energy band structures of monolayer and bilayer graphene were determined using first-principles with QUANTUM ESPRESSO [52]. The exchange correlation function was calculated using local-density approximation (LDA) [53] and the C.pz-hgh.UPF pseudopotential [54]. LDA usually underestimates the energy band gap. However, because both monolayer and bilayer graphene have zero band gap, LDA is suitable for obtaining the energy band structures of semimetals. We adopted a cutoff energy of approximately 80 Ry for plane-wave convergence and a  $k$ -points mesh of  $12 \times 12 \times 1$  for

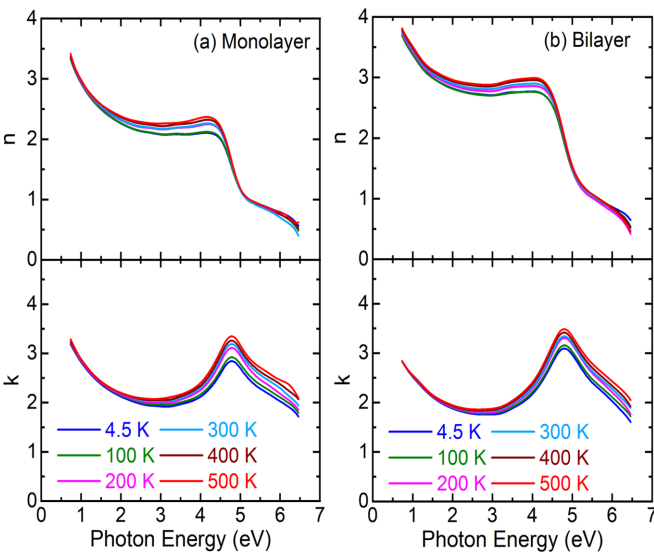


FIG. 1. Temperature-dependent refractive index (up) and extinction coefficient (bottom) spectra of (a) monolayer and (b) bilayer graphene.

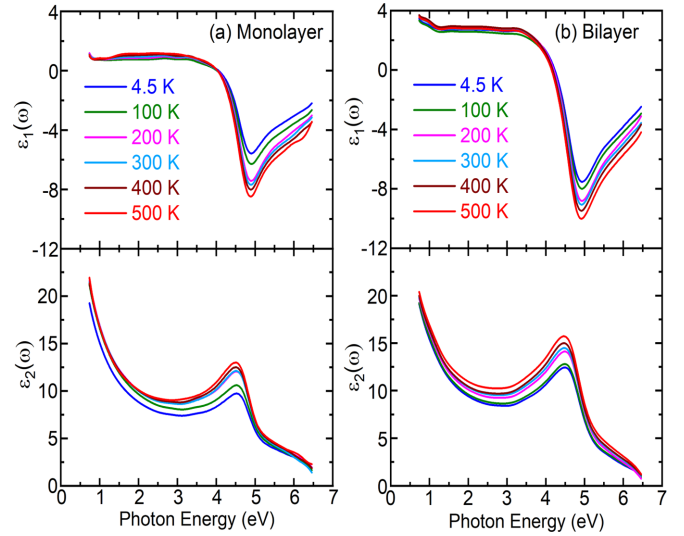


FIG. 2. Temperature-dependent complex dielectric function of (a) monolayer and (b) bilayer graphene.

the self-consistent field. For the non-self-consistent field, we used a larger  $k$ -points mesh of  $150 \times 150 \times 1$  and  $100 \times 100 \times 1$  for monolayer and bilayer graphene, respectively, to obtain the convergence of the dielectric function and joint density of state (JDOS). The real and imaginary parts of the dielectric function,  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$ , and the JDOS were calculated by using the EPSILON.X code in QUANTUM ESPRESSO within independent particle approximation (IPA). Compared with the many-body calculations, such as the Bethe-Salpeter equation (BSE), which considers electron-hole interactions and is a time-consuming calculation, IPA is more suitable for determining the optical properties of materials with photon energy of up to 30 eV; such high photon energy is observed in plasmonic excitation [7]. For bilayer graphene, we applied the rVV10 nonlocal correlation functional [55] for the van der Waals interaction. The optimized lattice structures were 2.432 and 2.436 Å for the monolayer and bilayer graphene, respectively; these values are consistent with the experimental value of  $\sim 2.46$  Å [56].

### III. RESULTS AND DISCUSSION

In Figs. 1(a) and 1(b), we present the temperature-dependent refractive index and extinction coefficient spectra of monolayer and bilayer graphene on sapphire substrates, respectively. Similar qualitative results were obtained for the samples on  $\text{SiO}_2/\text{Si}$  substrates, as depicted in Supplemental Material Fig. 2 [48]. These data are essential for understanding the optical response of photonic devices at various temperatures and photon energies. The refractive index of monolayer graphene at room temperature decreased with an increase in photon energy from the near-infrared to the visible frequency range. Two maxima were observed in the deep-UV region, corresponding to the anomalous dispersion region [57]. Moreover, the refractive index of bilayer graphene was larger in terms of magnitude than that of monolayer graphene. For both monolayer and bilayer graphene, the refractive index slightly increased with increasing temperature in the near-infrared

frequency range. The small increase in the refractive index as a function of temperature can be ascribed to enhanced electron-phonon interactions with increasing temperature, as observed for other semiconductors, such as Si, GaAs, and InP [58]. By contrast, the temperature variation of the refractive index was considerably larger in the deep-UV frequency range. In Fig. 1, we plot the extinction coefficient spectra of (a) monolayer and (b) bilayer graphene as a function of photon energy at room temperature. The extinction coefficient spectra exhibited a strong absorption and an additional shoulder in the deep-UV frequency range. Notably, the intensity of these two absorption peaks increased with increasing temperature.

Figure 2 depicts the temperature-dependent complex dielectric function of monolayer and bilayer graphene. The dispersion response of the real part  $\varepsilon_1$  of the complex dielectric function of monolayer graphene exhibited a positive value up to 4.0 eV at room temperature. This value then decreased to a negative value at approximately 4.89 eV. The photon energy at  $\varepsilon_1 = 0$  corresponds to the resonance condition of a plasmon. With an increase in temperature, the zero point redshifts, which reflects that the plasmon resonance zone became wider and deeper. This tunable optical response is beneficial for graphene-based plasmonic nanodevice applications. In Fig. 2, the optical transitions were identified in the spectra in accordance with resonance and antiresonance features that appeared at the same energy in the real and imaginary parts of the complex dielectric function, respectively. In particular, the imaginary part  $\varepsilon_2$  of monolayer and bilayer graphene was dominated by two optical transitions in the deep-UV frequency range. The intensities increased with increasing temperature. The bilayer graphene had an overall larger magnitude in the real and imaginary parts of the complex dielectric function than did monolayer graphene.

Figure 3 illustrates the optical absorption coefficient of (a) monolayer and (b) bilayer graphene as a function of photon energy at various temperatures. We calculated  $\alpha$  by using the complex dielectric function as follows,

$$\alpha = \frac{2\omega}{c} \sqrt{\frac{1}{2} \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)}, \quad (1)$$

where  $c$  is the speed of light in vacuum [59]. In Supplemental Material Fig. 3 [48], we compared the  $\alpha$  values of monolayer and bilayer graphene with that of single-crystal graphite at 4.5 K [7]. These spectra had three crucial features. First, the  $\alpha$  values of monolayer and bilayer graphene at room temperature gradually increased from the near-infrared to the visible frequency range. Both monolayer and bilayer graphene exhibited the maximum  $\alpha$  value in the deep-UV frequency region. The observed high optical absorption coefficient on the order of  $10^6 \text{ cm}^{-1}$  is desirable for efficient optical absorbers, such as photodetectors and photocatalysts. Second, the optical absorption coefficient spectra of monolayer and bilayer graphene exhibited a small dependence on temperature in the near-infrared and visible frequency range. By contrast, the  $\alpha$  value in the deep-UV range progressively increased with increasing temperature. We estimated that the total spectral weight would be constant at higher photon energies. Additional temperature-dependent optical measurements above 7 eV should be performed to confirm this assumption; however,

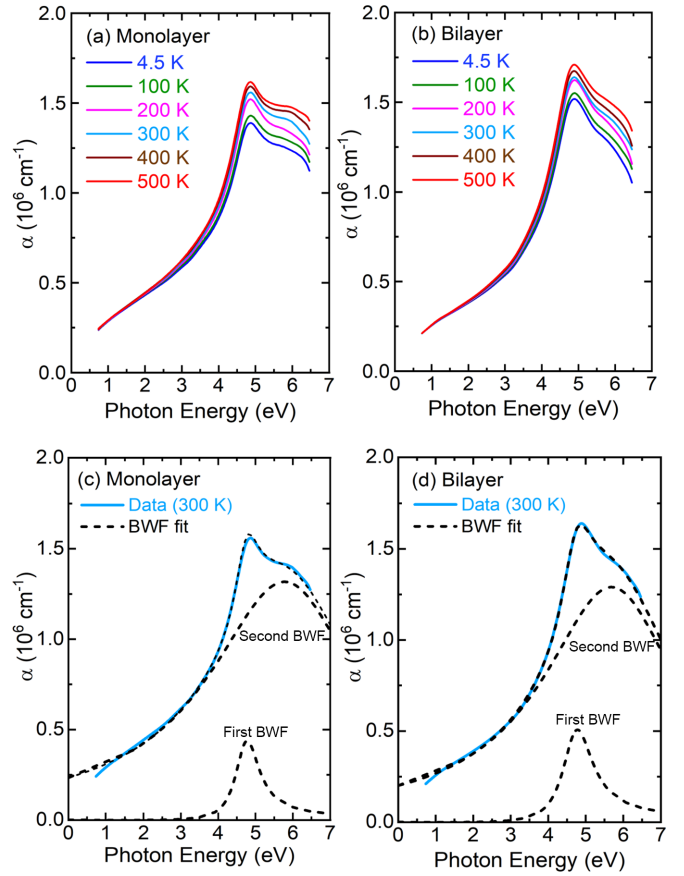


FIG. 3. Temperature-dependent optical absorption coefficient spectra of (a) monolayer and (b) bilayer graphene. (c) and (d) illustrate the fitting results of spectra obtained at 300 K by using the BWF model.

we performed measurements only up to 6.42 eV. Third, the optical absorption coefficient spectra of monolayer and bilayer graphene can be well fitted by two Breit-Wigner-Fano (BWF) components. The BWF formula is given by [7,60,61]

$$\alpha(\omega) = \alpha_0 \frac{[1 + \varepsilon(\omega)/q_{\text{BWF}}]^2}{1 + \varepsilon^2(\omega)}, \quad (2)$$

where  $\varepsilon(\omega) = (\omega - \omega_0)/\gamma$ ,  $\omega_0$  is the resonant energy,  $\gamma$  is the effective linewidth,  $\alpha_0$  is a prefactor, and  $1/q_{\text{BWF}}$  is the asymmetric factor of the BWF formula. The BWF formula describes the interference effect between the discrete spectra and continuum spectra of optical transitions [62]. When  $1/q_{\text{BWF}} = 0$ , Eq. (2) yields a Lorentzian function, which indicates the absence of interference. Constructive or destructive interference occurs above or below  $\omega_0$  depending on the sign of  $1/q_{\text{BWF}}$  and yields an asymmetrical line shape around  $\omega_0$ . The two BWF fitted curves to  $\alpha$  are presented for monolayer and bilayer graphene in Figs. 3(c) and 3(d) and the fitted parameters are listed in Table II. In Supplemental Material Fig. 4 [48], we compared the spectral weight ratio of the second BWF to the first BWF component in monolayer and bilayer graphene with that of single-crystal graphite at 300 K. It follows the single-exponential decay trend. Monolayer graphene exhibited a distinct second BWF component compared to bilayer graphene and single-crystal graphite.

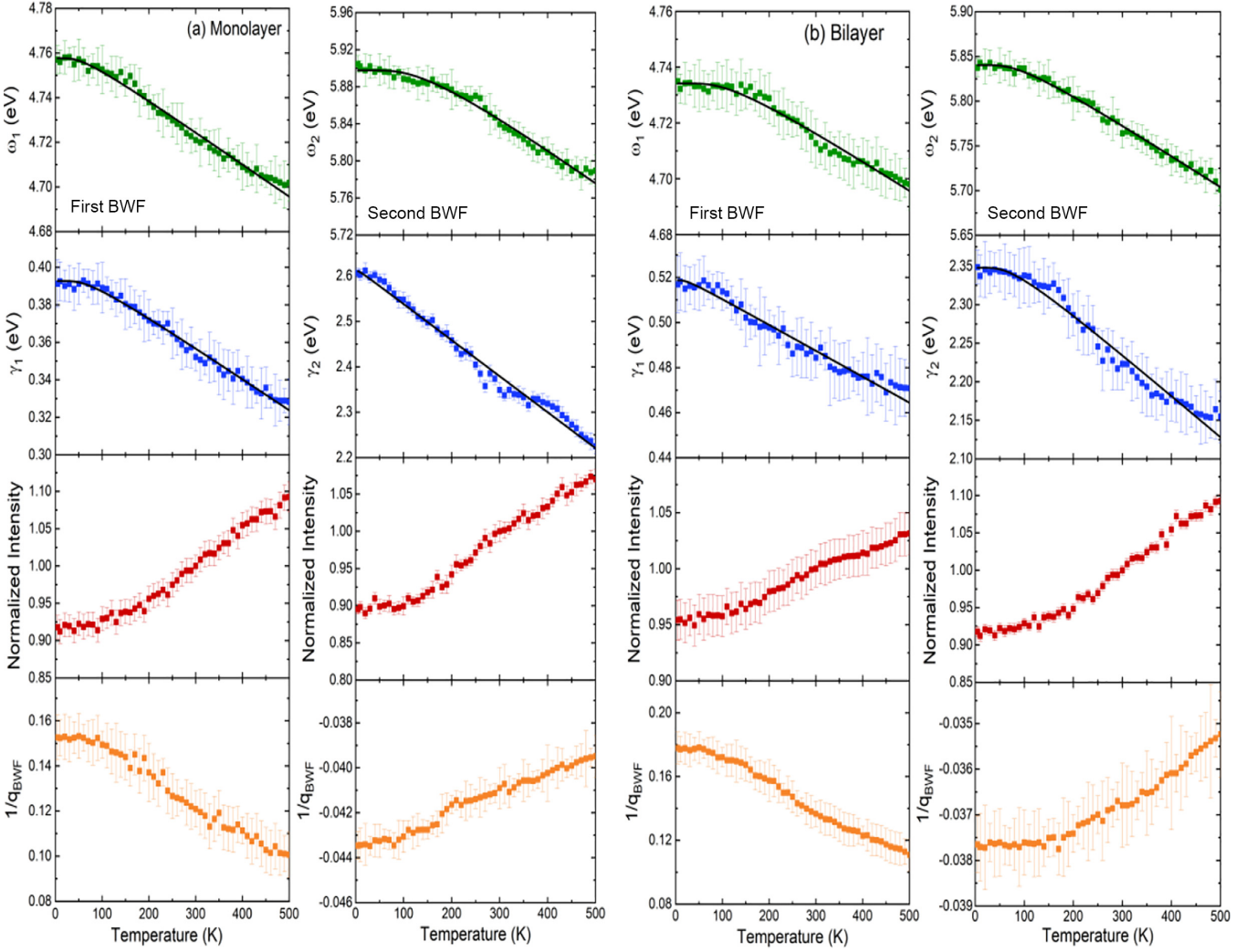


FIG. 4. Temperature-dependent peak energy, linewidth, normalized intensity, and asymmetric factor  $1/q_{\text{BWF}}$  of the first and second BWF components in (a) monolayer and (b) bilayer graphene.

In Figs. 4(a) and 4(b), we plot the peak energy, linewidth, normalized intensity, and asymmetric factor  $1/q_{\text{BWF}}$  as a function of temperature for the first and second BWF functions for monolayer and bilayer graphene, respectively. The dependence of all the parameters on temperature was similar between monolayer and bilayer graphene, except for  $1/q_{\text{BWF}}$ .

TABLE II. Fitted parameters of BWF to the optical absorption coefficient spectra of monolayer and bilayer graphene at room temperature.

Peak	Parameter	Monolayer	Bilayer
First BWF	$\omega_1$ (eV)	$4.728 \pm 0.005$	$4.712 \pm 0.002$
	$\gamma_1$ (eV)	$0.38 \pm 0.01$	$0.48 \pm 0.01$
	$\alpha_0$ ( $\text{cm}^{-1}$ )	$(0.43 \times 10^6) \pm 0.01$	$(0.49 \times 10^6) \pm 0.01$
	$1/q_{\text{BWF}}$	$0.12 \pm 0.01$	$0.13 \pm 0.01$
Second BWF	$\omega_2$ (eV)	$5.87 \pm 0.01$	$5.76 \pm 0.01$
	$\gamma_2$ (eV)	$2.44 \pm 0.01$	$2.22 \pm 0.01$
	$\alpha_0$ ( $\text{cm}^{-1}$ )	$(1.31 \times 10^6) \pm 0.02$	$(1.28 \times 10^6) \pm 0.01$
	$1/q_{\text{BWF}}$	$-0.04 \pm 0.01$	$-0.03 \pm 0.01$

With an increase in temperature, peak energy decreased, linewidth decreased, and normalized intensity increased. This temperature-dependent trend was stronger for monolayer and bilayer graphene than for single-crystal graphite [7]. Notably, the  $1/q_{\text{BWF}}$  values of two optical absorptions were positive and negative, respectively, indicating the difference in their intrinsic nature. The absolute values of two  $1/q_{\text{BWF}}$  of two BWF components decreased with increasing temperature, reflecting a decrease in the effect of the interference. The observed peak energy and linewidth under increased temperature were fitted by the Bose-Einstein model [63] as follows:

$$\omega(T) = a - b \left[ 1 + \frac{2}{e^{\frac{\Theta}{T}} - 1} \right], \quad (3)$$

and

$$\gamma(T) = \Gamma_0 \left[ 1 + \frac{2}{e^{\frac{\Theta}{T}} - 1} \right] + \Gamma_1, \quad (4)$$

where  $a$  and  $\Gamma_1$  represent peak energy and linewidth at 0 K, respectively;  $b$  and  $\Gamma_0$  are associated with the strength of electron-phonon interactions, and  $\Theta$  is the averaged phonon temperature. The solid lines in Figs. 4(a)

TABLE III. Fitted parameters of temperature-dependent peak energy and linewidth given by Eqs. (3) and (4) for two BWF components of monolayer and bilayer graphene.

Graphene	Peak	$a$ (eV)	$b$ (meV)	$\Gamma_0$ (meV)	$\Gamma_1$ (eV)	$\Theta$ (K)
Monolayer	First BWF	$4.77 \pm 0.01$	$14 \pm 2$	$-15 \pm 2$	$0.408 \pm 0.002$	$379 \pm 27$
	Second BWF	$5.97 \pm 0.01$	$75 \pm 10$	$-70 \pm 14$	$2.61 \pm 0.05$	$403 \pm 38$
Bilayer	First BWF	$4.75 \pm 0.02$	$17 \pm 3$	$-32 \pm 3$	$0.522 \pm 0.001$	$324 \pm 42$
	Second BWF	$5.88 \pm 0.01$	$44 \pm 4$	$-55 \pm 13$	$2.40 \pm 0.01$	$450 \pm 29$

and 4(b) represent the fitting using Eqs. (3) and (4). The fitted values are summarized in Table III. The  $b$  and  $\Gamma_0$  values were positive and negative, respectively, for both monolayer and bilayer graphene. The positive value of  $b$  indicated that the peak shifted to lower energy with an increase in temperature. The negative value of  $\Gamma_0$  reflected the long lifetime of electronic states for monolayer and bilayer graphene when temperature increased from 4.5 to 500 K.

The implications of optical data are discussed using the first-principles calculations. The observed two optical absorption spectra result from the combination of an excitonic transition at the saddle point ( $M$ ) in band structures, which is shown by the arrows at the  $M$  point in Figs. 5(a) and 5(b), and the collective excitation of surface plasmons [6,7]. The interference of the two optical absorption spectra is expressed

by the BWF asymmetric line shape, revealing single-particle electronic excitation coupled to the electronic continuum of plasmonic excitation. With an increase in temperature, the lifetime of surface plasmons decreases through Landau damping, in which a plasmon provides energy to an electron or a hole. Thus, the quantum interference effect between an exciton and a plasmon decreases, leading to (1) a decrease in the BWF asymmetric factor  $1/q_{\text{BWF}}$ , (2) a decrease in the spectral width  $\gamma$  of BWF, and (3) an increase in the peak intensity with an increase in temperature. The continuous spectra of surface plasmons become broad because of the decrease in the lifetime of the plasmon with an increase in temperature, resulting in smaller coupling with discrete single-particle excitation. This leads to an increase in the peak intensity. The observed temperature-dependent interference of excitonic and plasmonic excitations in monolayer and bilayer graphene

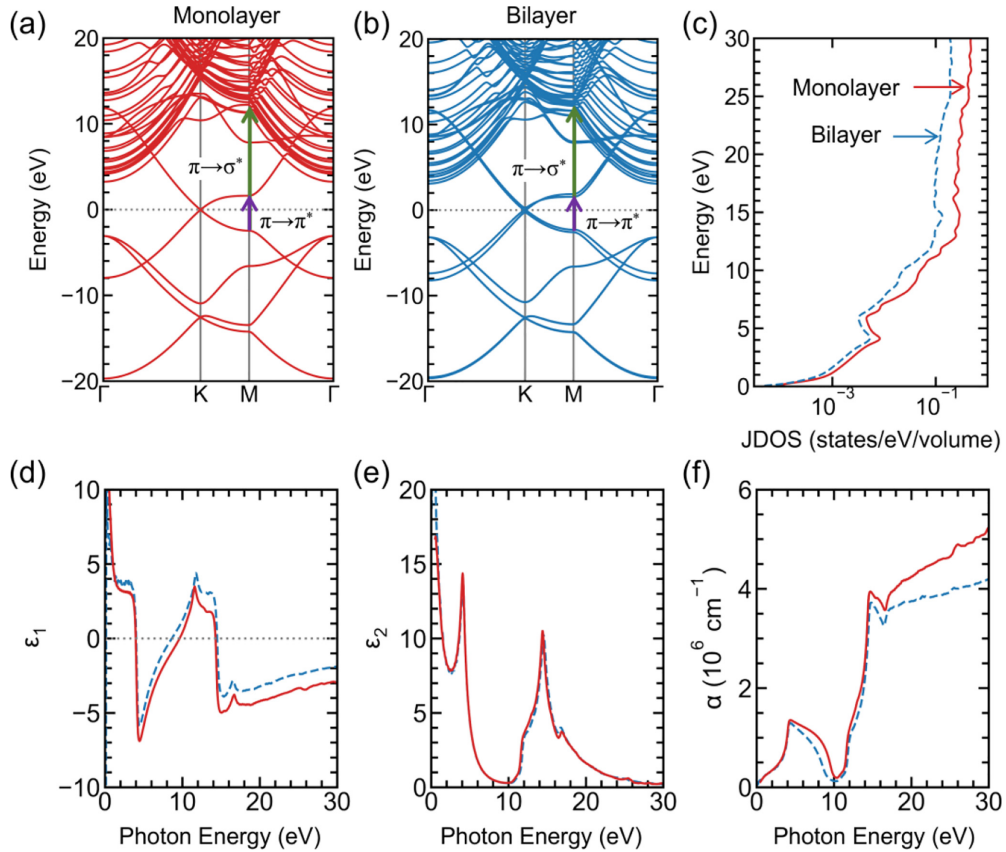


FIG. 5. Energy band structures of (a) monolayer and (b) bilayer graphene. The  $\pi \rightarrow \pi^*$  and  $\pi \rightarrow \sigma^*$  interband transitions at the saddle point  $M$  are denoted by purple and green arrows, respectively. (c) Log plot of the joint density of state (JDOS) of monolayer (solid line) and bilayer (dashed line) graphene. Calculated optical properties including (d) the real part  $\epsilon_1$ , (e) imaginary part  $\epsilon_2$ , and optical absorption coefficient  $\alpha$  as a function of photon energy for monolayer (solid line) and bilayer (dashed line) graphene.

was considerably larger than that in single-crystal graphite [7]. This finding can be explained by the strong dielectric and quantum confinement effects of electrons on the surface plasmon in 2D materials [6].

In Figs. 5(a) and 5(b), we plot the electronic energy dispersion of monolayer and bilayer graphene, respectively. The saddle point  $\pi \rightarrow \pi^*$  and  $\pi \rightarrow \sigma^*$  transitions at the high-symmetry  $M$  point of the Brillouin zone of monolayer or bilayer graphene lead to van Hove-like singularities of the JDOS at around 4.14 (4.17) eV and 14.77 (14.69) eV for monolayer (bilayer) graphene, respectively, as presented in Fig. 5(c). The JDOS is defined as [59]

$$\text{JDOS}(E) = \frac{1}{4\pi^2} \int d^3k [E_v(k) - E_c(k) - E], \quad (5)$$

where integration on the wave vector  $k$  is considered over the hexagonal 2D Brillouin zone, and  $E_v(k)$  and  $E_c(k)$  are the energies of the valence and conduction bands at  $k$ , respectively. The JDOS is enhanced when transitions from the flat valence band to the flat conduction band occur, as indicated by arrows in Figs. 5(a) and 5(b). The calculated JDOS peak at 4.1 eV, which corresponds to the  $\pi \rightarrow \pi^*$  interband transition, was smaller than the experimental value of around 4.7 eV (see Fig. 3). The energy difference can be explained by the effect of the electron-electron ( $e-e$ ) self-energy and the electron-hole ( $e-h$ ) interaction at the  $M$  point. By considering only the  $e-e$  self-energy within the GW method, Trevisanutto *et al.* [64] reported that the  $\pi \rightarrow \pi^*$  transition at the  $M$  point occurs at approximately 5 eV. By contrast, by using GW + BSE, which considers both  $e-e$  self-energy and  $e-h$  interaction, Yang *et al.* [30] indicated that the  $\pi \rightarrow \pi^*$  transition occurs at 4.5 eV, which is similar to that observed in this study. In the GW calculation [64], the  $\pi \rightarrow \sigma^*$  transition at the  $M$  point occurs at 15 eV, which is similar to the present IPA calculation for the  $\pi \rightarrow \sigma^*$  transition. Thus, the  $e-e$  self-energy effect might not be essential for the  $\pi \rightarrow \sigma^*$  transition.

In Figs. 5(d) and 5(e), we present the calculated real part  $\varepsilon_1$  and imaginary part  $\varepsilon_2$  of the dielectric function for monolayer (solid line) and bilayer (dashed line) graphene. Because the condition to obtain the peak of the optical absorption coefficient  $\alpha$  is  $\varepsilon_1 = 0$  and  $\varepsilon_2 \gg 1$  [see Eq. (1)], two peaks of  $\alpha$  are noted at 4.1 and 15 eV, as depicted in Fig. 5(f). The calculated  $\alpha$  value at 4 eV is approximately  $1.4 \times 10^6 \text{ cm}^{-1}$  for both monolayer and bilayer graphene, which is consistent with the experimental value of approximately  $1.5 \times 10^6 \text{ cm}^{-1}$  (Fig. 3). The calculated  $\alpha$  value for photon energy ranging from 0 to 7 eV agrees with the finding that the peak of monolayer graphene at 4 eV is more asymmetric than that of bilayer graphene (see the asymmetric factor  $1/q_{\text{BWF}}$  in Table II). By considering photon energy up to 30 eV, we determined a second peak of  $\alpha$  at 15 eV. The asymmetric behavior of the second peak might be due to the contribution of the  $\pi \rightarrow \sigma^*$  plasmon [64]. Experimentally determining the high value of photon energy, such as from 10 to 30 eV, is difficult. Thus, the theoretical calculations can explain not only the  $\pi \rightarrow \pi^*$  transition but also the  $\pi \rightarrow \sigma^*$  transition at high photon energy.

In Supplemental Material Fig. 5 [48], we show the calculated electron energy loss spectroscopy (EELS)  $[\text{Im}(1/\varepsilon)]$  as a function of photon energy for monolayer and bilayer

graphene. A peak consistent with the observed EELS by experiments for monolayer graphene [65], bilayer graphene [66], and graphite [67] is found around 5–6 eV as the  $\pi$  plasmon. Since  $\alpha$  is proportional to  $\varepsilon_2$ , the peak position of  $\alpha$  should coincide with the local maximum of  $\varepsilon_2$ . In Fig. 5(e), we found only one local maximum of  $\varepsilon_2$  at 4.1 eV. On the other hand, in Fig. 3,  $\alpha$  shows two peaks corresponding to two fitting BWF lines. These findings suggest that the first peak around 4.7 eV is related to the local maximum of  $\varepsilon_2$ , resulting from interband  $\pi \rightarrow \pi^*$  transitions, while the second peak around 5.8 eV is associated with the interband surface plasmon. In undoped graphene, both single-particle excitation and interband collective excitation can occur simultaneously, leading to an interference effect.

#### IV. SUMMARY

We combined spectroscopic ellipsometry and first-principles calculations to investigate the fundamental optical excitation of monolayer and bilayer graphene. The optical absorption spectra of monolayer and bilayer graphene at room temperature are expressed by two BWF components in the deep-UV frequency region, indicating an interference effect between discrete spectra and continuous spectra. We assigned the observed BWF resonances to an excitonic transition at the saddle point ( $M$ ) in band structures and collective excitation of the surface plasmons. These two BWF absorption spectra exhibited a redshift and narrowed under an increased intensity at elevated temperatures. This unusual temperature-dependent behavior can be attributed to a decreased quantum interference effect between the exciton and surface plasmons because of the damping of surface plasmons at the higher temperature. Our results not only provide microscopic insights into the quasiparticle band structures and collective excitations of graphene but also highlight the unique characteristics and potential of graphene for use in deep-UV optoelectronic and photonic device applications.

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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H.-L.L. conceived the research and was responsible for the experimental design. B.D.A. and D.P.G. conducted the experiments. P.S.-F., K.K., and H.A. were responsible for the sample preparation. N.T.H. and R.S. performed the first-principles calculations and theoretical analyses. H.-L.L., B.D.A., P.S.-F., N.T.H., and R.S. drafted the paper. All contributing authors discussed the results and provided their comments regarding the paper.

The authors declare no competing interests.

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