Anomalous K-Point Phonons in Noble Metal/Graphene Heterostructure Activated by Localized Surface Plasmon Resonance

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Supporting Information

ABSTRACT: The metal/graphene interface has been one of the most important research topics with regard to charge screening, charge transfer, contact resistance, and solar cells. Chemical bond formation of metal and graphene can be deduced from the defect induced D-band and its second-order mode, 2D band, measured by Raman spectroscopy, as a simple and nondestructive method. However, a phonon mode located at ∼1350 cm⁻¹, which is normally known as the defect-induced D-band, is intriguing for graphene deposited with noble metals (Ag, Au, and Cu). We observe anomalous K-point phonons in nonreactive noble metal/graphene heterostructures. The intensity ratio of the midfrequency mode at ∼1350 cm⁻¹ over G-band (∼1590 cm⁻¹) exhibits nonlinear but resonant behavior with the excitation laser wavelength, and more importantly, the phonon frequency–laser energy dispersion is ∼10⁻¹⁷ cm⁻¹ eV⁻¹, which is much less than the conventional range. These phonon modes of graphene at nonzero phonon wave vector (q ≠ 0) around K points are activated by localized surface plasmon resonance and not by the defects due to chemical bond formation of metal/graphene. This hypothesis is supported by density functional theory (DFT) calculations for noble metals and Cr along with the measured contact resistances.

KEYWORDS: graphene, noble metal, Raman, K-point phonon, localized surface plasmon

One- and two-dimensional sp² carbon materials have been one of the most important research subjects for several decades. In particular, these materials have been used as active and passive components of electrical and electro-optic devices as well as a platform for designing hybrid structures.¹⁻⁵ By choice of metal contacts, the electrical properties of field effect transistors (FETs) can be modulated by doping, Fermi-level pinning, Schottky barrier/Ohmic contact formation, etc.⁶⁻⁹ Recently, plasmonic structures or metamaterials were added to graphene channels to obtain amplified photoresponse at the desired wavelengths.¹⁰ Thus, the graphene/metal interface has been an important research...
topic to understand the electrical and optical properties of the related devices.

Up to now, theoretical calculations or electrical measurements, which provide only limited information at the interface, have been commonly utilized to investigate the graphene/metal interface.\textsuperscript{10–14} Raman spectroscopy has been a conventional nondestructive characterization tool, which is useful, in particular, for studying sp\textsuperscript{2} carbon species in terms of their
crystallinity, charge transfer, strain, or defects in conjunction with phonon frequency.

In this work, graphene/metal interaction in conjunction with chemical binding and charge transfer was investigated using a transparent substrate stacked with monolayer graphene and 7 different metal thin films, by Raman spectroscopy. We observed phonon modes of graphene through activated localized surface plasmons at nonzero phonon wave vector ($q \neq 0$) around K points. Density functional theory (DFT) calculations further confirmed that noble metals such as Ag, Au, and Cu did not exhibit binding with graphene, except Cr. With regard to studying the graphene/metal interaction, the contact properties of graphene/metal (Cu and Cr, similar work function) were compared with Raman results to determine the binding properties between graphene and Cu/Cr. Cu contact exhibited ~2 times higher contact resistance than Cr contact, which is in good agreement with the results of Raman studies.

RESULTS AND DISCUSSION

Figure 1a,b shows the typical Raman spectra of high crystal quality monolayer graphene grown by chemical vapor deposition (CVD) and defective graphene prepared by ultraviolet–ozone (UV–O3) treatment. The pristine graphene shown in Figure 1a exhibits two distinctive modes at ~1582 cm$^{-1}$ and ~2700 cm$^{-1}$, which are the G-band and 2D-band, respectively. In the UV–O3-treated graphene, an additional band appeared at ~1350 cm$^{-1}$, which is the defect induced “D-band”. The pristine monolayer graphene does not produce D-band but a very well-defined 2D band at the laser excitations in the range of 442–665 nm. This indicates that the CVD grown monolayer graphene is well synthesized in highly crystalline structure. The D-band and 2D-band are related to the interband process at K and K’ points, as shown in Figure 1c.15–17 In particular, the 2D band, which is the second order mode of D-band, is not involved with defects in the Raman process. Even though it is the second order mode, its intensity is considerably large due to the double resonance process. Thus, the defect induced D-band at ~1350 cm$^{-1}$ and its second order mode, 2D band at ~2800 cm$^{-1}$, are known as the indicators of crystallinity of sp$^2$ carbon materials. Furthermore, from the line shape of the 2D band, the number of thin graphite layers can be determined.18 It has been well-known for several decades that the frequency of D-band is dispersive by 50–60 cm$^{-1}$/eV, and the intensity ratio of D-band to G-band ($I_D/I_G$) is linearly proportional to the laser excitation wavelength.19,20 The density of defects and size of basal plane of graphene or graphite can be deduced from the modified Knight and White formula.19,20 From this formula, the grain size of our UV–O3-treated graphene is ~19 nm, as shown in Figure S1.

To understand the metal/graphene interactions, ~50 nm of seven different kinds of metal films (Cu, Ag, Al, Au, Pt, Ti, and Cr) was deposited on the graphene sample by E-beam and thermal evaporation, and the single layer graphene/metal film stacked on glass was directly observed by Raman spectroscopy, as shown in the schematics in Figure 2a. Here, the metals are categorized in two different groups: Noble metals such as Au, Ag, and Cu are known to have very weak interactions with graphene, and as a result, a van der Waals gap is formed at the interface. In contrast, Ti and Cr have strong interactions with graphene and form a covalent bond with graphene causing disorder in the sp$^2$ hybridized carbon system.21–24 Figure 2b,c shows Raman spectra of graphene deposited with these two groups of metals and bare graphene on SiO$_2$/Si substrate measured with 514 nm excitation as a reference. Four samples (Cu, Ag, or Au deposited graphene and bare graphene on SiO$_2$/Si substrate) were measured additionally with 642 nm excitation as shown in Figure 2d. Before metal deposition, the Raman spectrum of the graphene samples on SiO$_2$ substrate exhibits highly crystalline features. However, the Raman spectra of metal deposited samples show distinctive features, implying various degrees of chemical and physical interaction at the graphene/metal interface.

Figure 2b shows that Ti and Cr deposited graphene samples exhibit a sideband (D’-band, ~1650 cm$^{-1}$) at the G-band, which is related to the defect mediated intravalley Raman process at the $\Gamma$ point in graphene.16,17 Interestingly, the Raman spectrum of Cr deposited graphene exhibits extremely broadened D- and G-bands along with complete disappearance of the 2D band. This spectrum can be assigned to that of typical amorphous carbon. The D- and D’-band enhancement after metal film deposition on graphene can be attributed to various degrees of bond formation between metal and graphene. The intensity of the defect induced D-band (~1350 cm$^{-1}$) is well-known to be linearly proportional to the laser excitation wavelength.19,20 However, the samples comprising graphene deposited with noble metals, which have a weak interaction with graphene, exhibit unexpected Raman behaviors, as shown in Figure 2c,d. In particular, the D-band intensity at the graphene–Ag sample increases at low wavelengths up to 514 nm and decreases above 532 nm, resembling the plasmon resonance behavior. This anomalous behavior in the D-band intensity at different wavelengths cannot be explained using the defect-induced D-band, which depicts the linear relationship between the $I_D/I_G$ ratio and the excitation wavelength. The mode at ~1350 cm$^{-1}$ for the graphene–Ag sample, which is conventionally considered as D-band, can be attributed to the different origins of the ordinary defects. Not only the graphene deposited with Au, Ag, and Cu, but also the graphene deposited with Pt and Al exhibit unexpected D- and D’-band because these materials are known as nonreactive with graphene (see Supporting Information, Figure S2). To the best of our knowledge, there is no previous report of these anomalous phenomena in the literature.

To investigate the origin of the mid frequency mode at ~1350 cm$^{-1}$ of graphene deposited with noble metals, the Raman spectrum of graphene deposited with Ag, Au, and Cu were measured as a function of laser excitation wavelengths from 442 to 665 nm (~2.8 eV to ~1.85 eV), as displayed in Figure 3. The mode at ~1350 cm$^{-1}$ of metal deposited graphene will be still defined as D-band for convenience. All the Raman spectra were normalized to the G-band and evenly cascaded for better visualization. As clearly seen, the intensity ratio of the mid frequency mode over G-band intensity ($I_D/I_G$) is not linearly proportional to the wavelength of the laser excitation but seems to have different onset wavelengths.

Furthermore, the mid frequency mode of graphene deposited with Ag film completely disappeared for the 642 nm laser excitation. However, the $I_D/I_G$ ratio of graphene with intentionally created defects using UV–O3-treatment increases linearly with the laser excitation wavelength, as shown in Figure 1a. In addition, all the graphene samples deposited with noble metals show that the line shape of G-band is exceptionally broadened at a higher D-band intensity, and the absolute intensity of the overall Raman spectrum was significantly intensified by an order of magnitude. This is a typical phenomenon of Raman signal amplification due to localized
surface plasmon resonance (LSPR). This enhancement by surface plasmon enhanced Raman spectroscopy (SERS) has been reported by previous studies to be due to either electromagnetic field enhancement or chemical mechanism based on a charge transfer between the metallic surface and the graphene/carbon nanotubes.25,26

To understand the origin of the mid frequency mode at ~1350 cm\(^{-1}\) of graphene deposited with various metals, \(I_D/I_G\) and the frequency of D-band (\(\omega_D\)) were plotted as a function of the excitation laser wavelength and energy, respectively, in Figure 4a,b. As observed in Figure 3, \(I_D/I_G\) of graphene deposited with Ag, Au, and Cu was not linearly proportional to the excitation laser wavelength but exhibited resonant behavior. The frequency of D-band (\(\omega_D\)) has been reported to shift with the laser excitation wavelength by \(\Delta\omega_D/\Delta E \approx 51-60\) cm\(^{-1}\) eV\(^{-1}\) for graphite.15-17,19,20 The \(\Delta\omega_D/\Delta E\) value obtained from the Raman spectrum of our UV–O\(_3\)-treated graphene is found to be ~56 cm\(^{-1}\) eV\(^{-1}\) in Figure 4b, which is in good agreement with previous reports. However, \(\Delta\omega_D/\Delta E\) of Ag, Au, and Cu deposited graphene is in range of ~10-17 cm\(^{-1}\) eV\(^{-1}\). In particular, \(\Delta\omega_D/\Delta E\) of Ag deposited graphene seems to have two stages, and ignoring the lower energy part (less than ~2.0 eV), \(\Delta\omega_D/\Delta E\) of Ag deposited graphene becomes even lower to ~10 cm\(^{-1}\) eV\(^{-1}\). The origin of the mid frequency mode at ~1350 cm\(^{-1}\) of graphene deposited with noble metals is intriguing at this point because the \(I_D/I_G\) ratio is not linear but resonant; moreover, the frequency-energy dispersion, \(\Delta\omega/\Delta E\) is not in the conventional range of 51–60 cm\(^{-1}\) eV\(^{-1}\), established theoretically and experimentally.

The thinnest films (~2 nm) that can be controlled by our experimental setup were deposited for the study of graphene/metal interface because only nearest local structures of metals with graphene can significantly influence the physical properties.
of graphene. The optical absorption in UV–vis–NIR and the morphologies of 2 nm metal/graphene heterostructure observed by scanning electron microscopy (SEM) are shown in Figure 4c,d, respectively. The optical absorbance of the metal/graphene heterostructure measured in the UV–vis–NIR range is 526 nm (Ag), 652 nm (Au), and 770 nm (Cu), as shown in Figure 4e. Interestingly, the resonance wavelengths of the optical absorption spectra match well with the peak of $I_D/I_G$ ratio obtained for each metal in Figure 4a. We note that the strong absorption of the graphene sample deposited with 2 nm Cu film near the UV range is due to the oxidation of Cu nanoparticles. The oxide form of copper was confirmed by XPS measurement, as shown in Figure S3. A high resolution XPS spectra of Cu 2p shows that both Cu 2p3/2 and Cu 2p1/2 have shoulder peaks on the high binding energy side of Cu. This is strong evidence of oxide formation, and the peak positions of 933.9 and 954.0 eV appear at 770 nm. The LSPR resonances of 2 nm metal/graphene heterostructure measured in the UV–vis–NIR range is 526 nm (Ag), 652 nm (Au), and 770 nm (Cu), as shown in Figure 4c. These differences may originate from metal nanoparticle formation on graphene. More likely, the red shifts in the absorption spectra are due to the near-field coupling among noble metal nanoparticles. Nonmetallics are formed on graphene, and the results agree with those reported earlier.

Grains and part of apertures can be expected to remain after depositing 50 nm of Ag, Au, and Cu film. The morphologies of nanoparticles formed on graphene by 2 nm Ag, Au, and Cu thin film deposition were further investigated by atomic force microscopy (AFM), as shown in Figure S4. The height information for the nanoparticles can be obtained from the color scale bar on the right-hand side of the figure.

To understand the interface state of graphene and metal film, density functional theory (DFT) calculations have been conducted for the cases of Cr and noble metal, as shown in Figure 5a–d. To calculate the binding strength of metal nanoparticles on graphene surfaces, we selected the most spherical shape of the nanoparticle. For the cases of FCC metals (such as Ag, Cu, and Au), the minimal spherical shape is icosaedrons consisting of 13 and 55 atoms. The optimized geometry of the icosaedron of 55 atoms is presented in Figure 5a. The outermost surface consists of (100) and (111) surfaces, as indicated by a rectangle and triangle, respectively. Extensive studies on the binding of metal nanoparticles on carbon nanotube and graphene surfaces have been reported, and the equilibrium shapes of metal nanoparticles are not necessarily spherical. For example, gold nanoparticles can show flat monolayer geometry on a substrate. However, in the present work, instead of searching for a realistic geometry, we intended to estimate the binding strength of the metal particles on graphene surface. In the calculation with 13 and 55 spherical particles of Ag, Au, Cu, and Cr, only Cr shows a strong binding onto the graphene surface. Figure 5b shows the physisorption modes of Cu55 on graphene, which can be applicable to the cases of Ag and Au. For the case of Cr13 and Cr55, the binding energy, calculated from the total energy difference between the optimized structures shown in Figure 5c,d, is −1.30 eV and −3.81 eV, respectively. Because no binding is observed for the cases of Ag, Au, and Cu and by DFT calculations, the origin of mid frequency modes at $\sim$1350 cm$^{-1}$ is not associated with chemical bonding formation between noble metal and graphene. The series of experimental and theoretical evidence support that the anomalous D-band in graphene/noble metal is strongly related to the LSPRs, not activated by defect. The wavelength of free-space photon (\textasciitilde few hundred nanometers) is much longer than the length of lattice vectors, that is, very low momentum of photon; only $\Gamma$ point phonon (q = 0) can be activated among Raman active phonon modes. However, LSPRs can exist in even less than a few nanometers spaces. This kind of electromagnetic wave could obtain hundred times larger momentum than free-space photons, which may lead to assessment of phonons at $q \neq 0$. However, this unusual observation of dispersion values of noble metal deposited graphene seems to be controversial at this point, because the momentum of LSPRs of noble metals formed at the interface of graphene and metal film could be similar to that of defects, where no selection rules exist for this possible intervalley process at K point. Other Raman processes can also be considered to explain the abnormal Raman behavior of noble metal deposited graphene. This aspect needs to be clarified in the future.

From a practical viewpoint, the $I_D/I_G$ ratio measured by Raman spectroscopy is a strong parameter to investigate the actual chemical bonding between the graphene and metal. In this sense, the distinct origin of the D-band related to the localized surface plasmon, which appears at the contact between noble metals and graphene, may create confusion in understanding the defect formation in graphene. For a high-performance graphene FET, low contact resistance is a key parameter for effective electron injection from the metal to graphene. In the absence of covalent bonding between the metal and graphene, a van der Waals gap exists at the interface between metal electrodes and graphene, which results in an interfacial tunneling barrier. The strong interaction, which forms chemical bonds with graphene, strongly contributes to reduction in the contact resistance between graphene and metal. In order to verify the difference of two distinct origins of the D-band, we selected Cu and Cr as contact metals in the graphene FET, which have a similar work function of $\sim$4.5 eV but exhibit different binding characteristics as shown in Figure 5b,d. (Note: Raman spectra of the Cu and Cr deposited graphene samples are shown in Figure 2b (514 nm wavelength for the Cr contact) and Figure 3c (665 nm wavelength for the Cu contact), respectively)

Transfer length method (TLM) structure with various channel lengths was used to determine the contact resistance...
(\(R_\text{CNP}\)). Figure 6a shows the transfer curve of the graphene FET with channel length of 1 \(\mu\)m and channel width of 10 \(\mu\)m at a \(V_\text{ds}\) of 0.1 V. Both Cu and Cr contacts clearly show typical ambipolar behavior of graphene FET, and current saturation in the high \(V_\text{BG} - V_\text{CNP}\) region indicates better interfacial properties of the Cr contact. The transfer curve with different channel lengths is shown in the Supporting Information (Figure S5). For a low resistivity contact such as graphene/metal contact, TLM measurement is generally used to determine the contact resistance.39-41 Figure 6b shows the TLM resistance of the Cu and Cr contact at \(V_\text{BG} - V_\text{CNP} = 0\) V, where the slope indicates the sheet resistance (\(R_\text{sh}\)) of the graphene channel, and the contact resistance (\(2R_\text{c}\)) is estimated from the linear fitting curve of total resistance. The determination of contact resistance from TLM is based on the assumption of homogeneous \(R_\text{sh}\) of the channel area. The measured sheet resistance of our graphene device is about 12 k\(\Omega\)/sq, and it shows good homogeneity in all samples with a very small range of uncertainty of 2–3%, which may be induced by chemical residue. A lower \(R_\text{CNP}\) of 1.4 k\(\Omega\)/\(\mu\)m was obtained on the Cr contact compared with 2.8 k\(\Omega\)/\(\mu\)m of the Cu contact, and it decreased with increasing carrier concentration, as shown in Figure 6c. This result indicates that carrier injection barrier at the interface between Cr and graphene is lower than that between Cu and graphene, which is attributed to the different chemical bonding nature of the contact metals. The values of contact resistance of Cr-Graphene and Cu-Graphene are in a good agreement with the results of Raman measurements.

CONCLUSION

Graphene and metal interaction in terms of chemical binding and charge transfer can be investigated by Raman spectroscopy. However, the origin of the mid frequency mode at \(\sim 1350\) cm\(^{-1}\) of graphene can be ambiguous with regard to the formation of chemical bonds between graphene and metal. The \(I_\text{D}/I_\text{G}\) ratio of graphene deposited with Ag, Au, and Cu thin films exhibited extraordinarily nonlinear but resonant behavior. Its resonance wavelengths are largely similar to those of the optical absorption spectra in the UV–vis–NIR range of 2 nm Ag, 2 nm Au, and Cu–graphene heterostructure. We propose that the mid frequency mode (q \(\neq 0\)) is activated due to an intervalley process at K point involving localized surface plasmons instead of defects for momentum conservation and not by chemical bond formation between graphene and metal, which is supported by DFT calculations. The frequency-energy dispersion, \(\Delta\omega/\Delta E \sim \sim 10^{-27}\) cm\(^{-1}\) eV\(^{-1}\), which is considerably different from the value for sp\(^2\) carbon species including graphene/graphite (\(\sim 51–60\) cm\(^{-1}\) eV\(^{-1}\)). The frequency of the activated Raman mode at the same excitation energy is found to be roughly proportional to the energy of localized surface plasmons. In addition, \(R_\text{CNP}\) of the Cu–graphene device is approximately 2 times higher than that of the Cr–graphene device. This is due to their different chemical bonding nature, and the result is also consistent with the Raman spectrum results.

This work can provide insight for understanding the interfacial properties of metal/graphene contact and can be extended to general low-dimensional materials such as transition metal dichalcogenides (TMDs).

MATERIALS AND METHODS

Synthesis and Fabrication. To obtain high quality graphene flake, we performed preannealing to increase the grain size of the Cu substrate. We increased temperature up to 1070 °C for 40 min and then maintained it for 2 h. We flew 100 sccm hydrogen and 200 sccm Ar gases for cleaning the organic residue on the Cu surface. Subsequently, we kept the chamber closed until the temperature reached 1000 °C and then opened the chamber when the temperature was below 1000 °C. To decrease the surface roughness and organic residue, we performed polishing using Cu etchant (FeCl\(_3\), Taekwang Company, Korea). We use paper towel soaked in Cu etchant and DI water to rinse the Cu substrate. To remove the remaining humidity, we cleaned the surface with a N\(_2\) gun. For growing high quality graphene, we used low concentration methane gas (0.1% based Ar gas). Graphene was grown in 4 stages: ramping, annealing, growth, and cooling. We increased the temperature up to 1070 °C for 40 min because this temperature is near the Cu melting point in our CVD system. Then, we performed annealing at the same temperature for 30 min. Although we preannealed the Cu substrate, annealing is helpful for eliminating remaining organic molecules on the surface. Then, we use 3 kinds of gases (CH\(_4\), H\(_2\), Ar) for graphene synthesis. For forming graphene flake, we used 3 sccm methane, 16 sccm hydrogen (99.9999%), and 1000 sccm Ar gases (99.9999%) for 30 min. We opened the chamber when temperature was close to 1000 °C. Conventional E-beam lithography technique was used to define the device structure. The graphene channel width was 10 \(\mu\)m, and the channel lengths ranged from 200 nm to 1 \(\mu\)m. Cr (20 nm) and Cu (20 nm) as contact metal were deposited by E-beam evaporation and thermal evaporation at the pressure of 1 \(\times\) 10\(^{-4}\) Torr and Au (50 nm) was additionally deposited as a passivation layer on each sample. All device measurements were performed in a high vacuum condition of 3 \(\times\) 10\(^{-9}\) Torr.

Computation. We used the Vienna Ab initio Simulation Package (VASP) to calculate the ground state of many electron system in the framework of density functional theory.42-45 The plane-wave basis set with an energy cutoff of 400 eV, and the PBE-type gradient-corrected exchange-correlation potential was employed.46
**Measurements.** Raman spectra of the graphene samples were acquired using a Nanobase (XperRam 200) instrument equipped with various laser excitation wavelengths (442–665 nm). Electrical measurements were conducted in a vacuum probe station with 10⁻⁶ Torr at room temperature, equipped with Keithly 4200. XPS data of the copper film were acquired using a XPS/UPS system equipped with electron spectrometer (Scienta omicron R4000) with monochromatic Al Kα radiation powered at 2000 W under UHV (10⁻¹⁰ Torr) conditions at room temperature. For every core level measurement, 100 eV pass energy with 0.05 eV step was used.

**ASSOCIATED CONTENT**

**Supporting Information** The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.8b07761.

Raman spectra of graphene deposited with Al and Pt, Ip/Ip, ratio vs laser wavelength for UV–O₂-treated graphene, XPS spectra of Cu nanoparticles deposited on graphene, atomic force microscopy image of the 2 nm Au, Ag, and Cu deposited on graphene, and transfer curves for various channel lengths of graphene FET with Cu and Cr (PDF).

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**Notes**

The authors declare no competing financial interest.

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