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Optical properties of NbCl$_5$ and ZnMg intercalated graphite compounds

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Received 13 June 2014, revised 12 October 2014
Accepted for publication 20 October 2014
Published 13 November 2014

Abstract

We studied NbCl$_5$ and ZnMg alloy intercalated graphite compounds using an optical spectroscopy technique. These intercalated metallic graphite samples were quite challenging to obtain optical reflectance spectra since they were not flat and quite thin. By using both a new method and an in situ gold evaporation technique we were able to obtain reliable reflectance spectra of our samples in the far and mid infrared range (80–7000 cm$^{-1}$). We extracted the optical constants including the optical conductivity and the dielectric function from the measured reflectance spectra using a Kramers–Kronig analysis. We also extracted the dc conductivity and the plasma frequencies from the optical conductivity and dielectric functions. NbCl$_5$ intercalated graphite samples show similar optical conductivity spectra as bare highly oriented pyrolytic graphite even though there are some differences in detail. ZnMg intercalated samples show significantly different optical conductivity spectra from the bare graphite. Optical spectroscopy is one of the most reliable experimental techniques to obtain the electronic band structures of materials. The obtained optical conductivities support the recent theoretically calculated electronic band structures of NbCl$_5$ and ZnMg intercalated graphite compounds. Our results also provide important information of electronic structures and charge carrier properties of these two new intercalated materials for applications.

Keywords: graphite intercalation compounds, optical properties, electronic band structure

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

1. Introduction

Graphite intercalation compounds (GICs) were studied intensively in the 1970s and 1980s [1]. Recently, GICs have been revisited because they show interesting electronic and optical properties which are caused by graphene and few-layer graphene produced by intercalation [2–5]. Br$_2$ intercalated graphite shows supermetallicity which is attributed to graphene and few-layer graphene in the Br$_2$-GICs produced by intercalation [2, 3]. Usually the properties of GICs are determined by their intercalant species. For example, the c-axis conductivity of Br$_2$-GIC is decreased by a factor of 5 compared to pure graphite while that of K-GIC is increased by a factor of $\sim$25. Br$_2$ or H$_2$SO$_4$ intercalants produce more electrically isolated graphite planes and make the resulting GICs more electronically two-dimensional (2D) compared with pure graphite, while Li, K or Ca intercalant species integrate graphite layers and make them more electronically three-dimensional (3D) [1–3]. Since the discovery of a 2D carbon crystal, graphene [6], a new research boom on carbon-based compounds including graphite intercalation compounds has occurred [2, 3, 7–18].

In this study we used a ZnMg alloy and NbCl$_5$ as new intercalants and focused on infrared properties of GICs obtained with these two different intercalants. These two intercalants, NbCl$_5$ and the ZnMg alloy, have been theoretically predicted to be stably intercalated in graphite [1, 19]. These intercalated materials can be applied in a variety of fields combining the superconductivity of Nb and the great mechanical and
chemical stability of the ZnMg alloy respectively with the intriguing properties of graphitic materials [20]. These samples have been characterized by various experimental techniques: x-ray diffraction, scanning tunneling microscopy, x-ray photoelectron spectroscopy and the Hall current measurement [20]. Their band structures have also been obtained by using the density functional theory [20]. In our optical study we measured reflectance spectra of our samples since they show metallic behaviors. For the metallic samples, in general, reflectance spectra are more reliable than transmission ones to obtain the optical constants. We took reflectance spectra of our GIC samples and analyzed the measured reflectance spectra by applying a well-known Kramers–Kronig relation [21]. Through this analysis, in principle, one can obtain any optical constant. Here we obtained the optical conductivity and the dielectric function. We extracted the plasma frequencies of free charge carriers from the dielectric function and the dc conductivities and information of the electronic band structures from the optical conductivity. The theoretically calculated band structures of NbCl$_3$ and ZnMg intercalated graphite compounds are significantly different from each other [20]. The calculated band structures were not confirmed by experimental studies even though the Hall current measurement study showed their carrier types: NbCl$_3$ intercalated GIC has p-type carriers while the intercalated ZnMg alloy has n-type carriers. The optical spectroscopy study can provide important frequency-dependent properties, which are related to the electronic band structure. The extracted optical conductivities provide important evidence to qualitatively support the large differences in their calculated band structures. Additionally this infrared study provides useful information of these two new intercalated materials for various areas of applications.

2. Experimental

Our ZnMg alloy and NbCl$_3$ intercalated graphite compounds were prepared by using a two-zone vapor transport process. A detailed sample preparation procedure can be found elsewhere [20]. We used an optical spectroscopy technique to study infrared properties of our samples. We investigated four samples: two NbCl$_3$ and two ZnMg intercalated samples. We named our four samples as NbCl$_3$ 87 h and NbCl$_3$ 96 h for two NbCl$_3$ intercalated samples, and ZnMg 48 h and ZnMg 60 h for two ZnMg alloy intercalated ones. Here the numbers are the intercalating time periods of the samples in hours. Additionally we measured commercial bare highly oriented pyrolytic graphite (HOPG), which was purchased from SPI supplies (SPI-2 grade). We used a commercial fourier transform infrared (FTIR)-type spectrometer, Bruker Vertex 80 v to take reflectance spectra of our samples in the far- and mid-infrared range (50–7000 cm$^{-1}$) at room temperature. Since our samples were 20 µm thick free standing films and smooth but not flat as shown in figure 1(a) we had to develop a new method. In this new method we stretched and glued (with a 5 min epoxy) our floppy (20 µm thick) film on a 200 µm thick flat brass piece with an area of $\sim 2.5 \times 2.5$ mm$^2$ as shown in figure 1(b) to make the sample surface as flat as possible. After the epoxy was hardened we carefully tailored out the sample around the edges of the brass piece with a razor blade to make the sample square-shaped as shown in figure 1(c). We then attached the prepared film/brass sample on a sample cone as shown in figure 1(d) with the 5 min epoxy. Since the prepared sample surface was not completely flat as we can see in figure 1(c) we had to use an in situ gold evaporation technique [22] to obtain a reliable absolute reflectance spectrum. In this technique we coat a 200 nm thick gold film on the sample and use it as a reference of the reflectance. Since the thin gold film on the sample will have the same topology as that of the sample surface a rough sample surface can be corrected. Even though our samples showed quite weak signals due to rough (or not completely flat) surfaces of the samples we were able to get reliable spectra by extending the measurement time.

3. Experimental data and analysis

The measured in-plane reflectance spectra of our two NbCl$_3$ intercalated samples and bare HOPG are displayed in the top frame of figure 2 and reflectance spectra of two ZnMg intercalated samples and bare HOPG are shown in the bottom frame of figure 2. While two NbCl$_3$-GIC samples show similar reflectance spectra as the bare HOPG the reflectance spectra of two ZnMg-GIC samples deviate quite a lot from the bare HOPG reflectance in most of the spectral range of interest. In all reflectance spectra we can see a common feature which is an increase of reflectance with lowering the frequency. This common feature comes from contributions of the intraband transitions or the charge carriers in the systems and is directly related to the well-known Drude absorption. We note that our reflectance spectra are contaminated slightly by the epoxy which we used to attach the sample on the brass piece. The epoxy causes some sharp features between 1000 and 2000 cm$^{-1}$ and two broad dips between 3000 and 4000 cm$^{-1}$. We measured transmittance of the epoxy alone to make sure that the features come from the epoxy (not shown). In the insets of the top and bottom frames we display schematic sketches
of the crystal structures of NbCl$_5$-GIC and ZnMg-GIC nearby the intercalants.

We performed a Kramers–Kronig analysis to obtain optical constants including the optical conductivity and the dielectric function. To accomplish the Kramers–Kronig integration one has to extrapolate the measured reflectance spectra to both sides, zero and infinite frequencies [21]. For the zero frequency extrapolation of our metallic samples we used the Hagen–Rubens relation, i.e. $R(\omega) = 1 - A\sqrt{\omega}$, where $A$ is an appropriate constant related to the dc conductivity. For the extrapolation to infinity we used a measured reflectance spectrum of bare HOPG up to around 40,000 cm$^{-1}$ and above the frequency we used $R(\omega) = R(\omega_{\text{max}}) \omega^{-DE}$, where $\omega_{\text{max}}$ is the maximum frequency in the measured data file and $DE$ can be selected between 0 and 2. For above 10$^6$ cm$^{-1}$, where is in the free electron region, we used $R(\omega) = \frac{\omega}{P}$, where $P$ can be selected between 2 and 4. The real parts of the in-plane optical conductivities obtained from the measured reflectance spectra using the Kramers–Kronig analysis are shown in figure 3. All optical conductivities show metallic behaviors; they have finite dc conductivities. We observe quite a narrow absorption mode in all optical conductivity spectra at the low frequency region which comes from the intraband transitions or contributions of the charge carriers in the systems. In the insets we also show the calculated electronic band structures of NbCl$_5$ and ZnMg$_2$ intercalated samples using the density functional theory, which are reproduced from [20].

In the top frame of figure 3 we observe that the optical conductivity of NbCl$_5$ 87 h shows a similar shape as that of bare HOPG except below 1600 cm$^{-1}$, where it becomes roughly linearly frequency dependent. One can obtain the information of the electronic band structure from the optical conductivity. The optical conductivity shows the intraband transitions (Drude-like transitions) and the interband transitions, which are from filled bands to empty bands in the band structure. Above 1550 cm$^{-1}$ (marked with a red arrow) the optical conductivity becomes almost flat which indicates the interband transitions from the filled lower to the empty upper Dirac cones [11, 23–25]. As shown in the inset the calculated band structure shows additional flat bands below 0.4 eV which are absent in the bare HOPG band structure [24]. To understand the flat band contribution to the optical conductivity we simulate the optical conductivity spectra with two simple models.
of the electronic band structures shown in figure 4; model 1 (figure 4(a)) is the well-known Dirac cone band structure and model 2 (figure 4(b)) consists of a lower (or valence) Dirac cone and a flat conduction band. We note that the simulations were performed at $T = 0$ K. The real part of the in-plane normalized conductance ($G_1(\omega)$), which comes from contributions from the direct interband transitions, can be written as follows [21].

$$G_1(\omega) = \sigma(\omega) d_{\text{eff}} = \frac{e^2}{4\pi\varepsilon_0 m^*} \int d\vec{k} [\vec{a}_0 \cdot \vec{p}_{cv}^2 (\vec{k})] \delta (E_{cv} - \hbar\omega)$$

where $d_{\text{eff}}$ is the effective $c$-axis lattice constant of GIC or HOPG, $\vec{a}_0$ is the unit polarization vector, $\vec{p}_{cv}$ is the matrix element of the momentum operator, and $E_{cv} \equiv E_c - E_v$, i.e. the energy difference between the conduction and valence bands. $\varepsilon_1$ is the dielectric constant, which can be 1 here and $m$ is the electron band mass. $\vec{k}$ is the infinitesimal volume element in the wave vector space, here we consider the 2D circularly symmetric case $d\vec{k} = 2\pi d\vec{k}$. We also can define a mean square momentum operator as follows.

$$\langle [\vec{a}_0 \cdot \vec{p}_{cv} (\vec{k})]^2 \rangle = \langle p_{cv}^2 (k_x) \rangle + \langle p_{cv}^2 (k_y) \rangle = 2 \langle p_{cv}^2 \rangle$$

where $\langle p_{cv}^2 \rangle$ is assumed constant over the range of allowed $\vec{k}$ values. For the model 1 in figure 4(a) $E_{cv} = E_c - E_v = Ak - (-Ak) = 2Ak$, where $A$ is the slope in the Dirac cone, which can be related to the electron velocity ($v$) in the band, i.e. $A = \hbar v$. The resulting optical conductivity is as follows.

$$G_1(\omega) = \sigma(\omega) d_{\text{eff}} = \frac{e^2}{4\pi\varepsilon_0 m^*} \int_0^\infty k\delta (2Ak - \hbar\omega) d\vec{k}$$

In the last step we assumed that $\langle p_{cv}^2 \rangle \approx (mv)^2$. The calculated optical conductivity with the two Dirac cones is frequency-dependent, which is consistent of other studies [11, 23–25]. For model 2 in figure 4(b), which can be a simplified model for NbCl$_3$ intercalated graphite, $E_{cv} = E_c - E_v = E_0 - (-Ak) = E_0 - E_i + Ak$, where $A$ is the slope in the Dirac cone. The resulting optical conductivity is as follows.

$$G_1(\omega) = \sigma(\omega) d_{\text{eff}} = \frac{e^2}{4\pi\varepsilon_0 m^*} \int_0^\infty k\delta (2Ak - \hbar\omega) d\vec{k}$$

Here $\hbar\omega$ should be larger than $E_0$ for interband transitions. Since $E_0 \ll E_i$ there is an additional conductivity to the frequency-independent one. When $\omega$ becomes large enough the conductivity will be saturated to the frequency-independent value. In the inset of the upper frame of figure 3 we can see the Dirac cone feature with its apex energy ($E_i$) is around 0.4 eV and several flat bands below 0.4 eV. Since the most flat band levels ($E_f$) are pretty close to the apex energy ($E_i$), i.e. $E_f = E_i$, we expect that the frequency-independent transition will give a dominant contribution. Since there is a finite density of states in the Fermi level the intraband transition will contribute to the conductivity. The intraband transition will appear as the Drude mode in the optical conductivity i.e. $G_1(\omega) = G_1(0)(\omega^2 + F^2)$, where $F$ is the elastic impurity scattering rate between charge carriers. At room temperature the Fermi level will increase by the thermal excitations as results $E_f$ values measured from the Fermi level will be decreased. Therefore we expect that the optical conductivity will be similar to that of bare HOPG as we can see in our results. The linear frequency-dependent part of the observed optical conductivity cannot be explained clearly with this approach. In the measured conductivity spectra of NbCl$_3$ GICs (in the upper frame of figure 3) we also observe that the level of the frequency-independent optical conductivity decreases as doping increases. The level of the flat portion can be a measure of the effective (or averaged) $c$-axis lattice constant of a graphite intercalation compound [3]; the lower level means the larger effective $c$-axis constant. The doping dependence of the level is consistent with what we expected, i.e. as the doping increases the conductivity level is reduced.

In the bottom frame of figure 3 the real parts of the optical conductivity spectra of ZnMg 48 h and ZnMg 60 h are displayed along with that of bare HOPG. They show completely different frequency-dependent behaviors from those of the NbCl$_3$-GIC and bare HOPG. The conductivity spectra show neither the frequency-independent flat feature nor the frequency-linear one. The calculated band structure (in the inset) of NbMg intercalated graphite compound has neither the Dirac cone feature nor the flat band one. The calculated band structure shows a finite density of states in the Fermi level and many bands below (filled) and above (empty) the Fermi level. Therefore we expect at least an intraband transition (or the Drude) mode and interband transition modes within the spectral range of our data, up to $\sim$0.75 eV. As a result our measured optical conductivities support the theoretically calculated band structures of ZnMg intercalated graphite compounds [20] because they show an intraband absorption (or the Drude absorption) mode and interband absorption modes in the measured energy range.
In figure 5 we display the infrared active $E_{1u}$ in-plane modes of our four intercalated graphite samples along with our bare HOPG. Our two ZnMg-GIC samples show the same 3.5 cm$^{-1}$ blue-shift even though the amplitude of ZnMg 60 h is suppressed significantly. While NbCl$_3$ 87 h shows $\sim$1 cm$^{-1}$ blue-shift NbCl$_3$ 96 h shows a negligible amount of shift. The behavior seems to be consistent with results from a Raman study of the corresponding G peak of the same materials [20]; all samples show blue shifts and NbCl$_3$-GICs show smaller shifts than ZnMg-GICs. These results are indirect evidence to show that our samples are properly intercalated.

In figure 6 we display the dc conductivities of our four intercalated graphite samples and bare HOPG at room temperature estimated by two different ways: one is an extrapolation of the optical conductivity to zero frequency and the other is a direct measurement using a well-known four-probe transport measurement technique. The two sets of the dc conductivities show a similar material-dependent trend. The two sets of resulting dc values of ZnMg 60 h and ZnMg 48 h samples show slightly different intercalation-time dependent trends which may indicate that they have quite close dc conductivities. Both ways give consistent results for NbCl$_3$ 96 h and NbCl$_3$ 87 h samples. One can also calculate the dc conductivity with information of the mobility ($\mu$) and the charge carrier density ($N$), i.e. $\sigma_{dc} = \mu N e$, where $e$ is the elementary charge. By using the reported values of mobility and carrier density (table 1 in [20]) the calculated dc conductivities of NbCl$_3$ 87 h and ZnMg 48 h are 159 and 36 $\Omega^{-1}$ cm$^{-1}$, respectively. Even though the absolute values are different from what we obtained from the optical conductivities the relative values agree with our results. We note that bare HOPG gives a much higher dc conductivity than the value ($28 \Omega^{-1} $ cm$^{-1}$) which we get from the reported data (table 1 in [20]). One of the reasons why the two values are so different is that our bare HOPG shows a much higher (about 36 times) charge carrier density 3.6 $\times$ 10$^{19}$ cm$^{-3}$ than the reported value (9.8 $\times$ 10$^{17}$ cm$^{-3}$). To calculate charge carrier density from the plasma frequency we used the effective mass of HOPG 0.05 $m_e$ [26], where $m_e$ is the bare electron mass when we calculate the charge carrier density ($N$) from the plasma frequency, $\omega_p = \sqrt{4\pi Ne^2/m^*}$ (see figure 7 and the related text for the plasma frequency of the bare HOPG). Then our bare HOPG shows around a six times higher plasma frequency than the graphite in [20]. The large difference in the charge carriers may explain the large difference in the dc conductivities of our HOPG and the graphite in [20].

In figure 7 we display the real part of the dielectric function, $\varepsilon_1(\omega)$, as a function of $1/\omega^2$. The dielectric function for Drude charge carriers can be described by, approximately for a high frequency limit, $\varepsilon_1(\omega) \cong 1 - \omega_p^2 / \omega^2$, where $\omega_p^2 = 4\pi Ne^2/m^*$, $\omega_p$ is the Drude plasma frequency, $N$ is the charge carrier density, $e$ is the elementary charge, and $m^*$ is the band mass or effective mass. We can obtain the plasma frequency from the slope of the $\varepsilon_1(\omega)$ versus $1/\omega^2$ graph as shown in figure 7. In the inset we display the obtained plasma frequencies of our four samples and bare HOPG. The plasma frequency shows a similar sample dependent trend as in the dc conductivities (see

Figure 5. The infrared active $E_{1u}$ in-plane modes of our four intercalated graphite samples and bare HOPG.

Figure 6. The dc conductivities of our intercalated samples and bare HOPG are estimated by two different ways: one is an extrapolation of the optical conductivity to zero frequency and the other is a four-probe transport measurement technique.

Figure 7. The dielectric functions of our four samples and bare HOPG as a function of $1/\omega^2$. In the inset we show the material-dependent plasma frequencies obtained from the slopes ($-\omega_p^2$) in the dielectric functions. The (dark blue) star symbol indicates the plasma frequency value of the graphite extracted from [20].
figure 6). This may indicate that the dc conductivity is affected mostly by the plasma frequency. The extracted plasma frequency of NbCl$_5$ 87 h sample is larger than that of ZnMg 48 h sample. This result agrees with the reported values in [20].

4. Conclusions

We obtained reflectance spectra of NbCl$_5$ and ZnMg intercalated graphite compounds by using a developed method and an in situ gold evaporation technique. We analyzed the measured reflectance spectra using a typical Kramers–Kronig analysis to obtain optical constants including the optical conductivity and the dielectric function. The doping dependent behavior of the infrared active $E_{1u}$ in-plane modes seems to agree with results obtained from a Raman study of the corresponding G peak of the same materials [20]. Our extracted dc conductivities from the optical conductivities by extrapolating to zero frequency are consistent with the values obtained by direct dc transport measurements. We also extracted the plasma frequency of charge carriers from the dielectric function. The material-dependent plasma frequency agrees with reported results [20]. Finally the optical conductivities allow us to explain qualitatively the calculated electronic band structure [20] of the two intercalated graphite compounds with two different intercalants, NbCl$_5$ and ZnMg. These experimental results support the theoretically calculated band structure. Optical properties of these intercalated samples obtained in the study will provide useful information on applications of these materials.

Acknowledgments

JH acknowledges financial support from the National Research Foundation of Korea (NRFK grant No. 2012R1A1A2041150).

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