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Electrical conductivity and optical reflectance of potassium-intercalated graphitized poly(*p*-phenylene vinylene) films

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Potassium and sodium have been successfully intercalated into heat-treated poly(*p*-phenylene vinylene) films. Metallic characteristics were observed in these potassium-intercalated films by the measurements of the electrical conductivity and optical reflectance. The stage dependency of conductivity and other properties observed in these films are consistent with potassium-intercalated graphite as in highly oriented pyrolytic graphite. Sodium-intercalated film, which is very dilutely intercalated, also shows high electrical conductivity comparable to those of concentrated K-intercalated films and metallic temperature dependence.

I. INTRODUCTION

Graphite intercalation compounds (GIC's) have attracted much interest from both fundamental and practical points of view. Since the discovery of AsF_5- and SbF_5-intercalated graphites[1,2] with metallic conductivities higher than that of copper metal, extensive studies for various donor- and acceptor-type GIC's have been performed.[3] GIC's are also attractive as functional materials in practical applications such as electrical conductors,[4] storage of hydrogen,[5] batteries,[6] and so on. Most studies on GIC's have been performed using natural graphite, highly oriented pyrolytic graphite (HOPG), or Kish graphite as a host material. Other graphitic materials, except for the highly ordered benzene-derived graphite fiber (BDF),[7] are not functional as a host of GIC's, because many graphitic materials possess significantly lower crystalline perfection and lower electrical conductivity. The structural and physical properties on GIC strongly depend on the crystallinity of host graphitic material. In other words, to obtain GIC's, which have well-staged structure and metallic characteristics, high-quality graphitic material must be used as a host graphite.

On the other hand, as one of the preparative methods of graphitic materials, a heat treatment (pyrolysis) of an insulating polymer under inert gas has attracted much attention. There have been some studies on the nature of heat-treated polymers based on polyimides,[8] phenol-formaldehyde resin,[9] and poly(*p*-phenylene).[10]

Recently, Murakami *et al.*[11] have reported that by heat treatment poly(*p*-phenylene oxadiazole) film was converted to a graphite film. Furthermore, Ohnishi *et al.*[12] have also reported that graphite film can be obtained by heat treatment of poly(*p*-phenylene vinylene) film (PPV) prepared by the method of Murase *et al.*[13] These graphite films possess high electrical conductivity, comparable to those of HOPG (Ref. 14) and BDF.[7] Most recently we reported the detailed electrical conductivity and thermoelectric power of PPV films during graphitization.[15] However, the detailed properties of GIC's prepared from heat-treated PPV film have not been reported. Especially donor-type intercalation (intercalation with alkali metals) into graphitized films from insulating polymers has not been reported. Acceptors such as metal chlorides can be also intercalated into graphitized PPV films. Detailed properties on acceptor-intercalated films are given in the preceding paper.[16]

In this paper we report the fundamental properties, i.e., electrical conductivity, thermoelectric power, and optical reflectance of potassium-intercalated graphitized PPV films, comparing them with potassium-intercalated material prepared by use of the usual graphite hosts. Sodium-intercalated films as another donor-type intercalation are also investigated. For this peculiar intercalant (Na), which cannot be easily intercalated, some studies on synthesis and structure have been performed,[17] but the detailed electrical and optical properties have not been reported as far as we know. We also describe the electrical and optical properties on Na-intercalated films.

II. EXPERIMENTAL PROCEDURE

Poly(*p*-phenylene vinylene) (PPV) films were prepared by the method of Murase *et al.*[13] The pristine graphitized films were obtained by the heat treatment of PPV films at 2900 °C for 1 h in a high-purity Ar atmosphere. We have already reported the properties of PPV and graphitized PPV films.[15,18] In this study the graphitized PPV films with about 5 μm in thickness were used.

The intercalation of potassium was performed using the conventional two-zone vapor-transport method. For all reactions the potassium (K) temperature was kept at 250 °C. The host graphitized film temperature was set, depending on the desired stage, according to the report of Nixon *et al.*[19] In this study stage-1, -2, and -3 K compounds were prepared. A chemical formula of stage-1 K-intercalated film estimated by a weight-uptake method was C_8K. This formula is consistent with that of stage-1 compound of K and highly oriented pyrolytic graphite (HOPG) suggesting that the homogeneous K-

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intercalated films can be prepared from graphitized PPV films. For sodium intercalation, the temperatures of sodium and graphitized film were kept at 400 °C for several days.

For the electrical measurements, the graphitized film was cut out into small rectangular chips ($\sim 1 \times 10$ mm^2) and the electrical properties were measured along the film surface. The K-intercalated films for the electrical-conductivity measurement were prepared using Pyrex-glass reaction vessels with four tungsten (W) wires as electrodes. The film was placed across these W wires and fixed by four tiny drops of silver paint. Then intercalation of K into these films was carried out as explained above. The electrical conductivity was measured by a conventional four-probe technique. Detailed procedures of electrical measurements have been reported already in our previous paper.[15]

For the optical reflectance measurement, the K-intercalated films were prepared by utilizing the rectangular Pyrex-glass reaction tube. In the case of Na intercalation, the Na-intercalated film was transferred from the reaction ampoule to the rectangular Pyrex-glass cell under Ar atmosphere. The optical-reflectance measurement was carried out utilizing a monochrometer (JASCO CT-25A) and an optical-fiber technique and at near-normal incidence with unpolarized light.

III. RESULTS AND DISCUSSION

Figure 1 shows the relationship between the stage and the room-temperature electrical conductivity in K-intercalated graphitized films. By K intercalation, the conductivity at room temperature was enhanced by about 1 order of magnitude compared with that of the pristine graphitized film (8000 S/cm), and the highest conductivity of this K GIC was as high as 9×10^4 S/cm at the stage-3 compound. Furthermore, as is evident from this figure, this stage dependency of conductivity in the K-intercalated films coincides with that of HOPG-based K GIC.[20] The stage-2 and stage-3 compounds have higher conductivity than that of the stage-1 compound. The intercalation compounds with such a stage dependency and higher electrical conductivity have not been prepared from sheet-formed graphite (Grafoil).

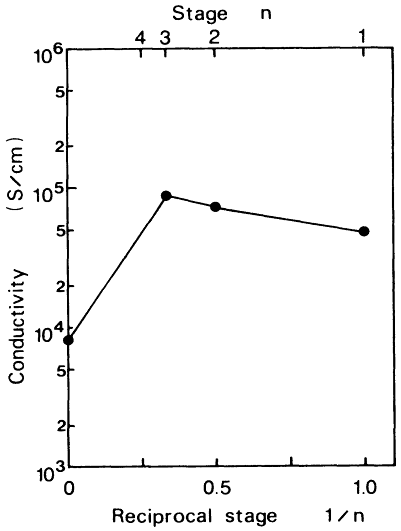

FIG. 1. Relationship between the stage and the room-temperature electrical conductivity in K-intercalated film.

However, the absolute value of conductivity at room temperature for these K-intercalated films was a little smaller than that of HOPG-based K GIC (2.5×10^5 S/cm for stage 3).[20] The reason why the electrical conductivity of this film is smaller than that of HOPG-based compound should be explained by the difference of the electrical conductivity between the host graphitic materials. The x-ray diffraction measurement for the pristine graphitized film indicates that the interlayer spacings (d_{002}) estimated by (00l) reflections ($l = 2,4,6$) are 3.36 3.36, and 3.37 Å, respectively. The interlayer spacing is equal to or longer than 3.36 Å and this value is a little longer than that of HOPG (3.354 Å), and the crystallite size along the c axis (L_c) is about 600 Å, which is much shorter than that of HOPG ($>$ 1000 Å). Namely, the graphitized PPV film has less crystalline perfection compared with that of HOPG. As a result of less crystal perfection, the electrical conductivity for the pristine film is smaller than that of HOPG. If intercalated films are synthesized from higher-quality graphite films prepared from a highly elongated PPV film, electrical conductivity as high as in HOPG-based GIC is certainly established.

Figure 2 shows the temperature dependences of the electrical conductivity for various stages of K-intercalated graphitized films contrasted with that of the pristine graphitized film. The electrical conductivity of the pristine graphitized film increases slightly with decreasing temperature and the maximum is observed at around 230 K.[15] On the contrary, K-intercalated graphitized films show a metallic temperature dependence of the electrical conductivity without regard to the stage. Such a stage-independent metallic behavior was observed also in K-intercalated HOPG.[20]

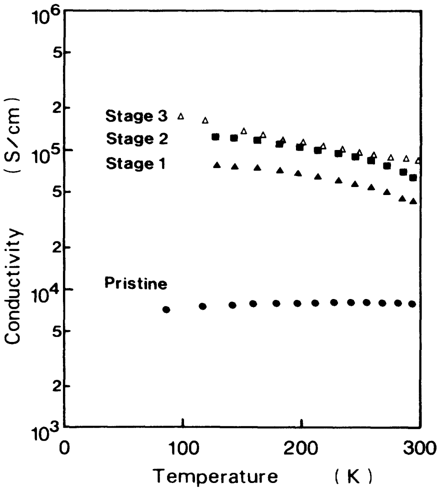

FIG. 2. Temperature dependences of electrical conductivity in the pristine and K-intercalated films.

Temperature dependence of the electrical conductivity in Na-intercalated film is shown in Fig. 3. The Na-intercalated film exhibited a room-temperature conductivity of 6×10^4 S/cm and also showed metallic temperature dependence of the electrical conductivity. A chemical formula derived from the weight-uptake method was $C_{62}Na$. The Na content in this film is similar to that of the stage-8 Na compound.[17] In spite of very dilute Na intercalation, the electrical conductivity for the Na-intercalated film is comparable to those concentrated K films (stages 1 and 2).

Temperature dependences of the thermoelectric power in the stage-1 and stage-2 K-intercalated graphitized films and Na-intercalated film are shown in Fig. 4. The thermoelectric power in both pristine and donor intercalated graphitized films were negative, indicating that the contribution from electron transport was predominant compared with that of hole conduction. During donor intercalation, the absolute value of the thermoelectric power at room temperature increased from 5 μV/K to 23 μV/K or 35 μV/K for K or Na systems, respectively, which indicates that the contribution of electron transport is greatly enhanced compared with hole transport after donor intercalation. There is no difference in the room-temperature thermoelectric powers between stage-1 and stage-2 K-intercalated films. These thermoelectric powers are the same values with those obtained for K GIC of the lower-stage compounds by Blackman *et al.*[21] prepared from well-oriented graphite formed by methane decomposition.

However, the temperature dependence of thermoelectric power in donor intercalated films is much different from those of the already reported HOPG-based stage-5 K intercalation and stage-2 $FeCl_3$-intercalation compounds.[22] In the reported HOPG-based intercalation compounds, the thermoelectric power was temperature insensitive in the range of 200 K $< T <$ 300 K.

On the other hand, metallic temperature dependence of thermoelectric power was observed for the K-intercalated graphitized films in the same temperature range as is evident from Fig. 4. The thermoelectric power decreases with decreasing ambient temperature.

Generally, the linear temperature dependence of thermoelectric power is known as characteristic of a nearly-filled-band metallic system. However, the slope of temperature dependence for stage 1 is larger than that for stage 2 and the extrapolated values at zero temperature do not cross with 0 μV/K. These results suggest that the temperature dependence of the thermoelectric power cannot be explained simply by a nearly-filled-band metallic system. Temperature dependence of thermoelectric power in the Na-intercalated film is also similar to that of K films. In the acceptor-type GIC, the temperature dependence of thermoelectric power was qualitatively explained by considering both a diffusion term and a phonon-drag term according to Sugihara.[23] In the detailed analysis of thermoelectric power for these donor intercalated films, a phonon-drag effect should also be taken into consideration.

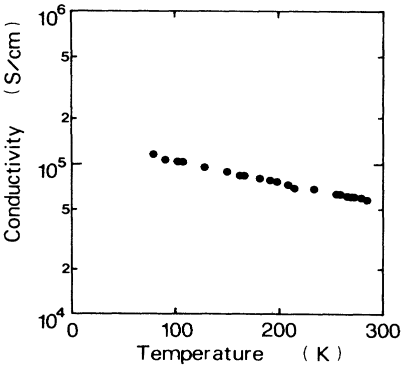

FIG. 3. Temperature dependence of electrical conductivity in Na-intercalated film.

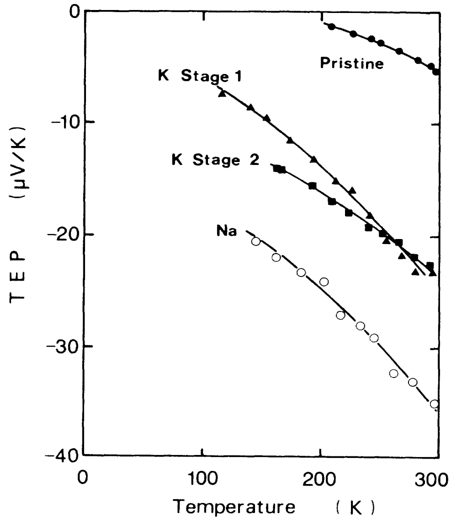

FIG. 4. Temperature dependences of thermoelectric power (TEP) in the pristine, K-intercalated, and Na-intercalated films.

The mechanism for such a metallic temperature dependence of thermoelectric power in these intercalated films is not clarified in this stage. For the future, thermoelectric power measurements for the various-stage intercalation compounds prepared from the materials with various degree of crystalline perfection are needed.

Drastic color changes were observed with alkali-metal intercalation into graphitized PPV films. In this study we obtained golden and blue lustrous films for the stage-1 and stage-2 K-intercalation compounds, respectively, analogous to HOPG. The optical reflectances for the pristine and K-intercalated films are shown in Fig. 5. The reflectance (R) of the pristine film decreased slightly with increasing photon energy. On the other hand, the sharply defined plasma edges, which have been associated with the classical plasma resonance of free carriers, were observed for K-intercalated films, indicating metallic behavior. The minimum in reflectance was observed at about 1.7 eV for stage 2. This minimum shifted to higher photon energy (2.7 eV) for stage 1. These results are also consistent with those of HOPG-based K compounds.[24] The Na-intercalated film was of the same color and appearance as a graphitized film itself. The plasma edge could not be observed in our investigated photon energy range although the reflectance spectrum

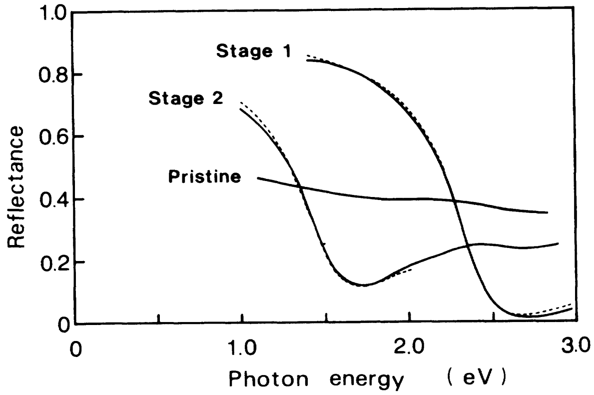

FIG. 5. Optical reflectances of the pristine and stage-1 and stage-2 K-intercalated films. The dashed line is the fitted curve by the two-carrier model with the parameters in Table I.

shifted down from the spectrum of the pristine film ($R \sim 0.4$) to $R \sim 0.3$.

The obtained reflectances for the K-intercalated films were analyzed by using a simple one-carrier Drude model. The evaluated optical parameters by the Drude fitting are summarized in Table I.

Assuming that the scattering time (τ) is the same at dc and optical frequencies, the conductivity (σ_{opt}) in optical frequency can be derived from these optical reflectances. For the stage-1 and stage-2 K-intercalated films, the σ_{opt} were estimated to be 1.2×10^4 and 0.6×10^4 S/cm, respectively. These σ_{opt} values are not in agreement with the dc conductivities (σ_{dc}). The stage dependency, as in the case for the dc conductivity, was not obtained. These results of the one-carrier Drude fitting are consistent with those of HOPG-based Rb GIC.[25] It suggests that the simple one-carrier Drude model is not suitable in this case, and the multicarrier system for these alkali-metal–intercalated graphitized films should be taken into consideration.

Therefore, the obtained reflectance curves for the intercalated films were refitted using a two-carrier model. In this analysis the core dielectric constant (ϵ_{core}) obtained by one-carrier fitting was used, and the two plasma frequencies (ω_{p1}, ω_{p2}) were related with the plasma frequency from the one-carrier system by the following equation:

$$\omega_p^2 \sim \omega_{p1}^2 + \omega_{p2}^2 \ .$$

This fitting method is similar to that of Rb HOPG by Guerard *et al.*[25]

The optical parameters obtained by these procedures were also summarized in Table I. Though the value of τ_2 was not sensitive in this fitting, the reflectance curve was reproduced by taking 10^{-13} s order of magnitude in τ_2 and the value of σ_{opt} was in agreement with σ_{dc} for both stage-1 and stage-2 compounds. These τ_2 values are comparable to those for Rb HOPG (Ref. 25) and to that derived from one-carrier model for AsF_5 HOPG.[26] For such analysis the galvanomagnetic data are needed, which are lacking in this stage. Furthermore, assuming that the effective masses are invariable between stages 1 and 2, the ratios in carrier density of stage 1 to stage 2 were evaluated to be 1.6 and 1.4 for the two types of carrier. The carrier density for stage 1 is roughly 1.5 times as high as that for stage 2. However, the stage-2 compound has higher dc conductivity than that for the stage-1 compound. This result suggests that the average mobility for stage 1 is reduced from that for stage 2. This reduction of the average mobility is consistent with the results in alkali-metal–intercalated HOPG for magnetoresistance measurements.[20,25]

However, at least these spectral data indicate that the K intercalation can be successfully performed into graphitized PPV films and real metallic films can be obtained just as the case of K-intercalated HOPG.

IV. SUMMARY

The electrical conductivity, thermoelectric power, and optical reflectance have been examined in donor-type intercalated graphitized films prepared by the heat treatment of poly(p-phenylene vinylene) films. The result of this study can be summarized as follows.

(1) K atoms can be successfully intercalated into the graphitized films prepared by the heat treatment of poly(p-phenylene vinylene) films as in HOPG, and the various stages of compounds were obtained. Na atoms, which are most difficult intercalant, can be also intercalated into these films.

(2) The electrical conductivity was much enhanced by K intercalation. The room-temperature electrical conductivity of stage-2 and stage-3 K-intercalated films is higher than that of the stage-1 compound. This stage dependency is similar to those of HOPG-based compounds. Even though the intercalation was very diluted,

TABLE I. Drude parameters for stage-1 and stage-2 K-intercalated graphitized films.

Parameter	Stage 1		Stage 2	
	One	Two	One	Two
ϵ_{core}	7.4		11.7	
ω_p (eV) or ω_{p1} (eV)	6.6	5.7	5.3	4.5
ω_{p2} (eV)		3.3		2.8
$\tau(s)$ or τ_1 (s)	1.3×10^{-14}	1.0×10^{-14}	1.0×10^{-14}	7.0×10^{-15}
τ_2 (s)		1.7×10^{-13}		4.1×10^{-13}
σ_{opt} (S/cm)	1.2×10^4	4.4×10^4	0.6×10^4	7.0×10^4
σ_{dc} (S/cm)	5×10^4		7×10^4	

the electrical conductivity in the Na-intercalated film was also much enhanced and was comparable to that of the concentrated K-intercalated films (stages 1 and 2).

(3) The thermoelectric power in K-intercalated films of stages 1 and 2 was around $-23\ \mu V/K$, indicating dominant contribution of electron transport. The linear temperature dependence of thermoelectric power was obtained in this K-intercalated film, contrary to that of reported stage-5 K HOPG. In the case of a dilute Na compound, a large negative thermoelectric power and a linear temperature dependence were also observed.

(4) These K-intercalated graphitized films indicated the metallic behavior in the temperature dependences of electrical conductivity and optical reflectances.

(5) The analysis of the optical reflectance spectrum with a sharp plasma edge by using a simple one-carrier Drude model is not in agreement with the dc conductivity for both stage-1 and stage-2 K-intercalated films. This result should suggest that the multicarrier system is also appropriate in these intercalated films. On the other hand, in the Na-intercalated film the plasma edge was not observed in our investigated photon energy range though the reflectance spectrum shifted down from the spectrum of the pristine graphitized film.

(6) Though the properties on intercalated graphitized PPV films are very similar to those of HOPG-based compounds, the detailed properties are under the influence of less crystal perfection.

(7) These results also clearly indicate that the K-intercalated metallic graphitized materials were obtained in the form of film for the first time.

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