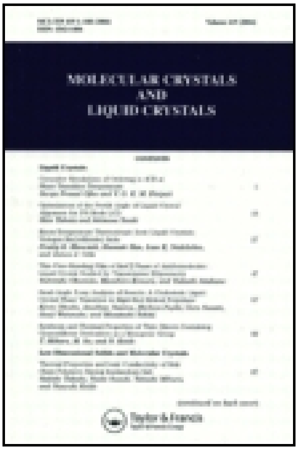

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Kinetics of Intercalation of Br_2 or ICl into Pyrolytic Graphite "NIKAFILM" Studied by Thermoelectric Properties

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The kinetics of intercalation of halogen molecules Br_2 or ICl into pyrolytic graphite "NIKA-FILM", a commercial product of Nihon Carbon Inc., has been studied by the measurement of electron transport phenomena, especially the thermoelectric properties. The data were analyzed by a two-carriers band model, and it was concluded that the change in the resistivity and Seebeck coefficient is due to the increase in the positive hole density because the intercalant halogen molecules work as acceptors. From the weight increment the stage index was tentatively estimated to be four, and the deduced charge transfer rate was 1.33×10^{-4} e/molecule.

Keywords: intercalation; graphite; bromine; iodine monochloride; Seebeck coefficient

INTRODUCTION

Bromine and iodine monochloride are known as typical intercalants to graphite, and the in-situ measurements of the electrical properties such as resistivity, Hall coefficient and the magneto-resistance were performed by one of the authors[ST][1]. Present work is a continuation to the former work and is done with an aim to clarify the behavior of the electronic state during the reaction time more thoroughly by making a measurement on the thermoelectric properties.

It was revealed that the pristine host material, NIKAFILM, has a positive Seebeck coefficient of about $+4\mu V/K$, and it increases with the reaction time, and finally reaches a saturation value of over $+20\mu V/K$, after a reaction time of $6x10^4s$, showing a tremendous change by the halogen intercalation. The data were analyzed by a two-carriers band model.

EXPERIMENTAL PROCEDURE

The conventional method of intercalating halogen molecules into NIKAFILM adopted in the former work has been followed in the present study on the whole. A NIKAFILM sample of a thickness of 1mm was cut into a rectangular form of say 5x30 mm and current and potential leads, and for thermopower measurement a heater as well, were attached to the sample. The sample was hung over the solution of Br_2 or ICl diluted with CCl_4 20 to 60 times, a few cm above the surface of the liquid. The measurement was made during the whole reaction time up to the maximum of $6x10^4s$. Data were taken automatically every second using HP362.

In order to investigate the electronic structure of the pristine NIKAFILM the temperature dependence of electrical resistivity, Hall coefficient, magneto-resistance coefficient and the Seebeck coefficient were measured from 90 to 300K.

EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of the electrical resistivity, magneto-resistance coefficient and Hall coefficient of NIKAFILM. Contrary to the single crystal graphite, in which the electrical resistivity increases almost linearly with temperature showing a metallic or semi-metallic behavior of conduction, the resistivity of NIKAFILM decreases slowly with increasing temperature. The magneto-resistance coefficient also shows a slow decrease with increasing temperature, suggesting a weak temperature dependence of the carrier mobilities. Hall coefficient is negative over the whole temperature range of measurement and shows a slower temperature dependence. Figure 2 is the result of the measurement of Seebeck coefficient. It takes a negative and very small value, about $-1\mu V/K$, at the lowest temperature, and increases with increasing temperature, levels off at around 160K at the value of +5μV/K, continues taking this value up to 280K, and then begins to decrease slowly, but the value remains positive at the highest temperature of measurement.

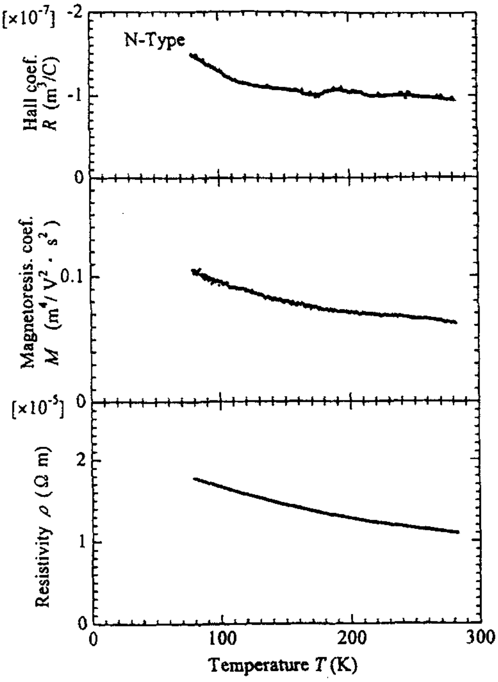

Fig. 1
Temperature dependence of resistivity (bottom), magneto-resistance coefficient (middle), and Hall coefficient (top) of NIKAFILM.

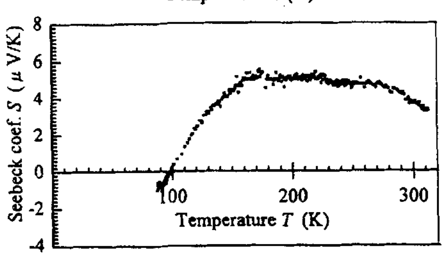

Fig. 2
Temperature dependence of Seebeck coefficient of NIKAFILM.

Figure 3 shows the results of the Seebeck coefficient measurement during the reaction time of intercalation of Br_2 or ICl into NIKAFILM. In Br_2 intercalation the degree of dilution was varied in order to get a rough idea of the effect of vapor pressure. Two levels of dilution were adopted, and the difference between them was conspicuous. For the 20 times dilution (top diagram), Seebeck coefficient increases rapidly by intercalation, and saturates to a value of 20μV/K at 2000s time of reaction, while for the 30 times dilution (middle diagram), it increases more slowly and continues increasing up to 5x10^{4}s, and saturates to 25μV/K. The effect of ICl intercalation is similar to Br_2 but still slower.

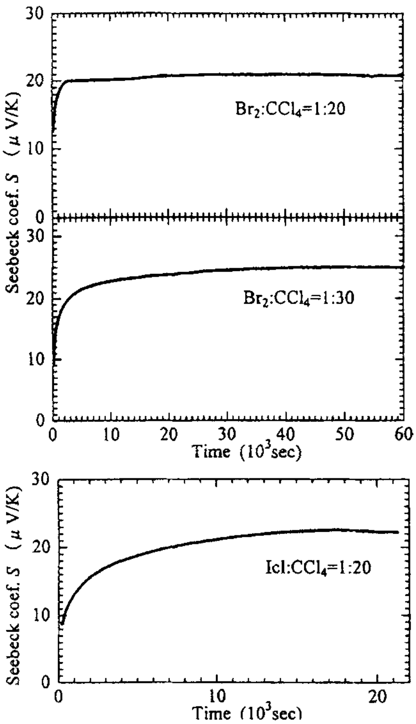

Fig.3
Variation of Seebeck coefficient due to intercalation.
Upper two are Br_2 intercalation and the bottom one is ICl.

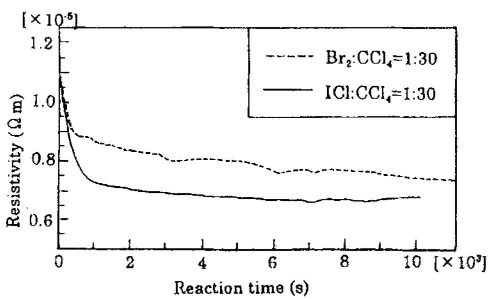

Fig.4
Variation of electrical resistivity due to intercalation, Br_2 and ICl.

Figure 4 is the result of resistivity measurement. In either case, Br_2 or ICl, the resistivity decreases by halogen intercalation. The effect of intercalation is larger than that of Br_2.

DISCUSSION

According to a two-carrier band model for a semiconductor (and for a semi-metal as well), the density of conduction electrons and holes, n and p respectively, are expressed as follows:

$$n = \frac{4\pi}{h^3} (2m_e^* kT)^{3/2} F_{1/2}(\xi_e) \quad (1)$$

$$p = \frac{4\pi}{h^3} (2m_h^* kT)^{3/2} F_{1/2}(\xi_h), \quad (2)$$

where h, k, T are the Planck constant, Boltzmann constant and the temperature, respectively. The effective mass of an electron and a hole are written as m_e^* and m_h^*, and the reduced Fermi energy for them, ξ_e and ξ_h, are defined as E_F/kT and $(-E_G - E_F)/kT$, where E_G and E_F are the band gap (positive for a semiconductor and negative for a semi-metal) and the Fermi energy. Functions such as $F_{1/2}(\xi_e)$ mean Fermi-Dirac integrals.

The mobility of the electrons and holes are written as μ_e and μ_h, respectively. Introducing two parameters, α and β which mean the mobility and carrier density ratio as defined $\alpha = \mu_h / \mu_e$ and $\beta = p / n$, we can neatly express the conductivity σ, Hall coefficient R and magneto-resistance coefficient M as follows:

$$\sigma = e\, n \mu_e (1 + \alpha\beta) \quad (3)$$

$$R = (1/n\, e)(-1 + \alpha^2\beta) / (1 + \alpha\beta)^2 \quad (4)$$

$$M = \mu_e^2\ \alpha\beta\ (1+\alpha)^2/(1+\alpha\beta)^2\ . \quad (5)$$

The Seebeck coefficient S is expressed as a weighted mean of contributions from electrons, S_e, and that from holes S_h as

$$S = (S_e + \alpha\beta S_h) / (1 + \alpha\beta), \quad (6)$$

while S_e is given by

$$S_e = \frac{k}{e} \left\{ \frac{(s + 5/2)\ F_{s+3/2}(\xi_e)}{(s + 3/2)\ F_{s+1/2}(\xi_e)} - \xi_e \right\}, \quad (7)$$

and S_h similarly. Here, s is a scattering factor, and is assumed $-1/2$.

Using equations from (3) to (6) and making a best fitting to the experimental results of corresponding quantities we are able to determine material constants for the energy bands relevant to the transport phenomena in NIKAFILM, *i.e.*, the band gap and effective masses. They are: $E_G = -45meV$, $m_e^* = 0.1\ m_0$ and $m_h^* = 0.1\ m_0$, where m_0 is the electron mass.

Now we consider the effect of intercalation. We assume that mobilities of carriers are not affected by the intercalation, and we calculate n, p, S and other quantities as functions of E_F, using equations (1), (2) and (6). By equating the so calculated S to the observed values of S the variation of E_F with respect to the reaction time is determined, and also is determined the variation of carrier density n and p. They are shown in Figure 5. The intercalant Br_2 acts as an acceptor, and lowers the Fermi level resulting in the increase in holes and decrease in electrons. From the measurement of the weight increment due to intercalation the stage index has been estimated to be four. The change in the carrier densities permits the estimation of charge transfer rate, giving $1.33x10^{-4}$ e/molecule, which is unexpectedly small. But it is very near to the value obtained formerly[1], $1.39x10^{-4}$ e/molecule, which was derived from the analysis of data of resistivity, Hall and magneto-resistance coefficient.

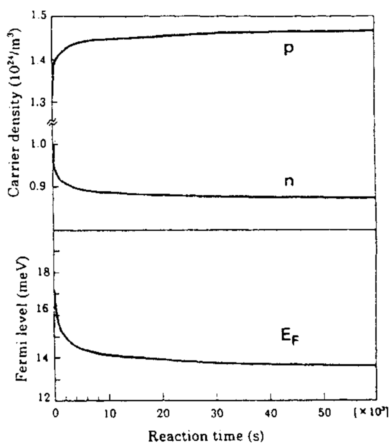

Fig.5
Calculated variation of Fermi level and carrier densities with reaction time.

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[1] S. Tanuma, Report of the work by a grant-in-aid for Scientific Research from Japan Ministry of Education, No.01460036,(1996)p28.