CHARACTERIZATION OF CARBON FILMS PREPARED FROM POLYIMIDE FILMS AT DIFFERENT HEAT-TREATMENT TEMPERATURES AND THEIR INTERCALATION BEHAVIOR

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Introduction

Graphite intercalation compounds (GICs) have higher electrical conductivity, lower thermal conductivity, larger Seebeck coefficient than those of host graphite. These values are also depending on those of host graphite. Moreover, the structure and property of graphite/carbon materials strongly depend on the heat-treatment temperature (HTT). In this study, we aim to control the properties of GICs by using carbon films at different HTTs. Herein, we determine the structure and properties of host carbon films and their HTT dependence. Furthermore, intercalation behavior and the properties of resulting products are explained.

Materials and Methods

Five types of carbon films were prepared by pyrolysis of poly(4,4'-oxydiphenylene-pyromellitimide) (PMDA-ODA) polyimide films (KANEKA Apical® 75AH; thickness: 75 µm) at HTT of 1600, 2000, 2400, 2600, and 2800 °C under inert gas atmosphere. The film structures were characterised by X-ray diffraction (XRD) and Raman spectra. The electrical conductivity (σ), thermal conductivity (κ), and Seebeck coefficient (S) were measured at room temperature by a four-terminal method. In addition, Hall coefficient (R_H) and magnetoresistance ($\Delta\rho/\rho$) were measured by a five-terminal method at 25 °C, and the conductive carrier density (n_e, n_h: e: electron, h: hole) and mobility (μ_e, μ_h) were estimated. Furthermore, the intercalations of potassium (K) and molybdenum chloride ($MoCl_5$) into carbon films were performed. A mixture of K or $MoCl_5$ and C was added to the glass reaction tube at a molar ratio of 1:8 [K:C or $MoCl_5$:C], and the tubes were sealed after they were vacuumed. The reaction tubes were heated at 250 °C for K and 300 °C for $MoCl_5$ for 3 days. After the reaction products were exposed to air, the XRD patterns were obtained and electrical conductivity was measured. For some products, thermal conductivity, Seebeck coefficient, Hall coefficient, and magnetoresistance were also measured. For comparison, a commercial graphitized polyimide film (Panasonic, PGS®) and a graphite sheet obtained from natural graphite (NeoGraf, Grafoil®) were used as host carbon.

Results and Discussion

Figure 1 shows the electrical conductivity, thermal conductivity, Seebeck coefficient, Hall coefficient, and magnetoresistance against HTT of carbon films. The interplanar spacing (d_{004}) estimated from the XRD pattern are also shown in **Figure 1.** For Hall coefficient and magnetoresistance, the values obtained at 0.4 T were plotted. The XRD patterns and Raman spectra showed that the major structural change occurred at HTT of 2000 °C. The electrical conductivity and thermal conductivity had a same relationship with HTT, although the thermal conductivities of the films with low HTTs were remeasured. The Seebeck and Hall coefficients had identical relation with HTT, whose signs are affected by the major carrier (electron or hole). These coefficients changed depending on the HTT; they had the largest positive values at 2400 °C and small negative values at 1600 °C and 2000 °C. This behavior is similar to those reported in a previous study[1]. Magnetoresistance was strongly affected by film structure; its values for the films at 2000 °C were slightly negative, which indicate that the carbon film is turbostratic.

Table 1 shows the estimated electron density, hole density, and mobility of carbon films at 25 °C. The density values were similar, while mobility considerably increased with HTT. In the case of the film of HTT 2000 °C, the estimation of the above-mentioned properties was impossible because magnetoresistance was negative.

For the lower HTT films, intercalation did not occur. The minimum HTT was 2000 °C for K and 2400 °C for $MoCl_5$. The films of HTT 2000°C after the reaction with K (K-HTT2000) had a bronze color and the XRD patterns did not change before and after intercalation. In contrast, the films of higher HTT had a bright gold color and stage 1 structure. However, because the Seebeck coefficient of K-HTT2000 was -16 μVK^{-1} while that of the host film was +6 μVK^{-1}, it was confirmed that intercalation occurred.

For the films of HTT 2400 °C, after the reaction with $MoCl_5$, a very small peak attributed to the intercalated structure was observed in the XRD pattern; however, it disappeared in a day.

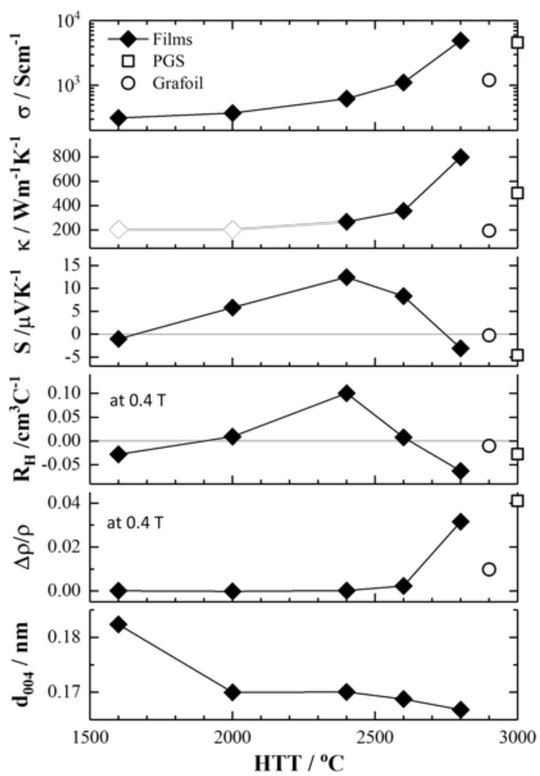

Figure 1. Electrical conductivity (σ), thermal conductivity (κ), Seebeck coefficient (S), Hall coefficient (R_H), magnetoresistance (Δρ/ρ), and interplanar spacing (d_{004}) of the films

Conclusions

Five carbon films were prepared by pyrolysis of polyimide films at HTTs of 1600–2800 °C and characterized. Their structures drastically changed around 2400 °C, thereby changing their properties. Moreover, intercalation became difficult in the carbon films having HTT below 2400 °C.

Table 1. Electron density (n_e), hole density (n_h), and mobility (μ) of the carbon films

HTT/°C	n_e/cm^3	n_h/cm^3	μ/cm^{2}V^{-1}s^{-1}
2800	3.6×10^{18}	3.1×10^{18}	4500
2600	3.2×10^{18}	3.2×10^{18}	1200
2400	4.5×10^{18}	6.5×10^{18}	320
1600	6.5×10^{18}	5.8×10^{18}	170

References

1. Hishiyama Y., Igarashi K., Kanaoka I., Fujii H., Taneda T., Koidesawa T., Shimazawa Y., Yoshida A. (1997). Graphitization behavior of kapton-derived carbon film related to structure, microtexture and transport properties. *Carbon* 35, 657-668