GRAPHITE FILMS FROM POLYIMIDES III. PROPERTIES OF FILMS

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Introduction

The polyimide films with rigid imide molecules and high degrees of their orientations along the film surfaces have been known to be good precursors for obtaining graphite films through simple heat treatments without high pressure[1-7]. In their preparation suitable heating rate[7] and a holding at 2100-2300°C[4] were preferable. These graphite films show similar behavior in galvanomagnetic properties, such as transverse magnetoresistance $\Delta\rho/\rho$ and Hall coefficient R_H, when their crystallinity including preferred orientation of graphite layers along the film surface is almost the same.

Structural changes of carbonized films by heat treatments

The starting materials were commercially available polyimide films Kapton (25 μm in thickness) and Novax (25 μm in thickness), and a laboratory prepared polyimide film (PMDA/PPT/TAB, denoted hereafter as PPT, 45 μm in thickness)[8,9]. These polyimide films were sandwiched between polished artificial graphite plates and carbonized in flowing nitrogen in infrared heating apparatus at 900°C for 1 hr with heating rates 120-200°C. Carbonized films were sandwiched again between polished artificial graphite plates and heat-treated in a graphite resistance furnace in pure argon at temperatures between 1800 and 3200°C. For carbonized films of Kapton, heat treatments above 2400°C were made with holding at 2300°C for 30 min, while heat treatments above 2200°C for carbonized films of Novax and PPT with pre-treatment at 2100°C for 30 min. Structural evolution of the carbonized films by heat treatments was examined by X-ray diffraction on film specimens. The dependence of interlayer spacing d_{002} on heat treatment temperature (HTT) indicated that graphitization behaviors of carbonized films of Novax and PPT were similar with the same HHT of 2200°C for initiation of graphitization[9,10]. On carbonized films of Kapton, graphitization started at HTT around 2300°C[11]. At HTTs above 2400°C, however, the dependence of d_{002} on HTT was exactly the same for these films. For the specimens heat-treated at 3000°C, d_{002} values were the same ones of 0.3355 nm, indicating capability of preparation of high quality graphite films from these carbon films by successive heat treatments at temperatures higher than 3000°C.

Galvanomagnetic properties

Figure 1 shows transverse magnetoresistance (magnetic field B perpendicular to the film surface) measured at 77 K and under a magnetic field of 1 T for the carbonized films of Kapton, Novax and PPT plotted as a function of HTT[8,9]. For the films heat-treated above 2800°C, similar behavior of the transverse magnetoresistance was measured irrespective of the starting material. Negative magnetoresistance was observed for Kapton carbon films with HTTs bellow 2350°C, for Novax carbon films with HTTs below 2120°C and for PPT carbon films with HTTs below 2180°C. The absolute values of the negative magnetoresistances of Kapton carbon films are smaller than those measured for Novax and PPT carbon films. Hall coefficient measured at 77 K and under a magnetic field of 1 T was negative for the specimens with d_{002} values smaller than 0.3375 nm.

The graphite films prepared by heat treatments above 3100°C show behaviors in the dependencies of transverse magnetoresistance and Hall coefficient on magnetic field measured at 77 K similar to those measured for compression annealed pyrolytic graphites[12]. Figures 2 and 3 exemplify the data on magnetoresistance and Hall coefficient for various graphite films together with those obtained for pyrolytic graphite and HOPG[3,13]. In high magnetic fields and at temperatures below 4.2 K, all of these graphite films reveal Shubnikov de-Haas oscillations in transverse magnetoresistance and Hall coefficient[3]. Figure 4 shows examples of the Shbnikov de-Haas oscillation in Hall coefficient measured at 4.2 K. The Landau levels for majority carriers could be assigned, as indicated by 3e and 3h (majority electrons and holes with n = 3, respectively), for example, in Fig. 4, indicating high crystallinity of these graphite films.

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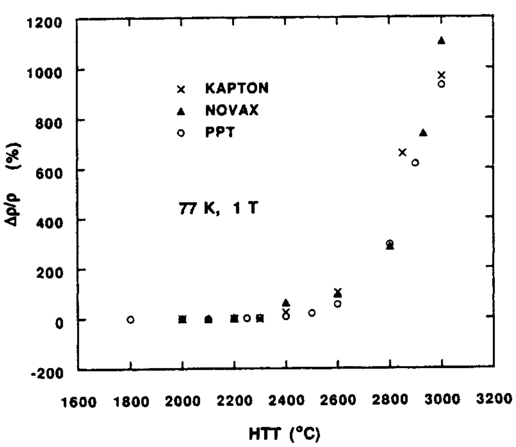

Figure 1 - Transverse magnetoresistance measured at 77 K and under a magnetic field of 1 T for the carbonized films of Kapton, Novax and PPT plotted as a function of HTT[8,9].

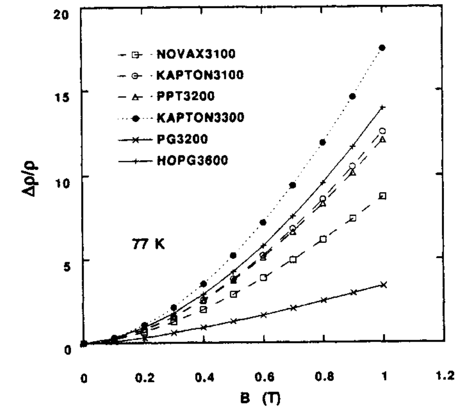

Figure 2 - Transverse magnetoresistance for various graphite films measured at 77 K[3,13].

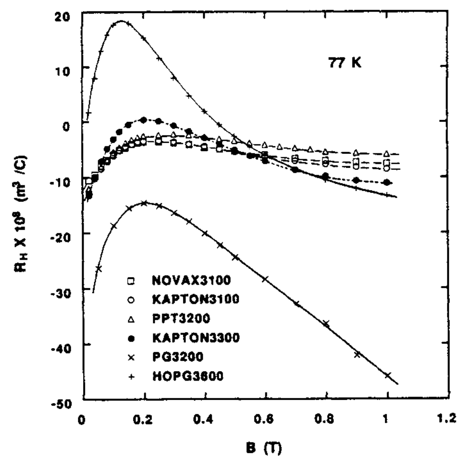

Figure 3 - Hall coefficient for various graphite films measured at 77 K[3,13].

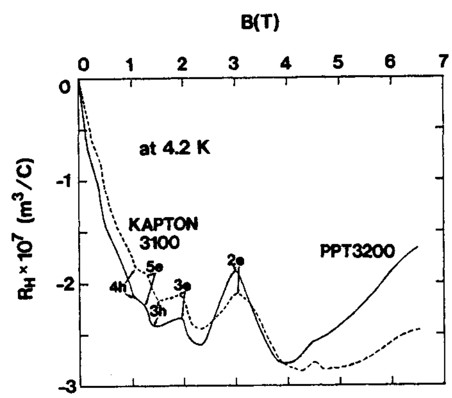

Figure 4 - Examples of Shubnikov de-Haas oscillation observed in Hall coefficient[3].