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Structure and properties of highly crystallized graphite films based on polyimide Kapton

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Highly crystallized graphite films were prepared by heat treatment of carbonized polyimide films (Kapton) at temperatures of 2700 and 3050° C. Interlayer spacing d_{002} at room temperature, and electrical resistivity, magnetoresistance and Hall coefficient at room and liquid nitrogen temperatures were measured. All of these data indicate high crystallinity of the graphitized Kapton films obtained. For the graphite films heat treated at 3050° C mean-square mobilities were estimated from the magnetoresistance data at 1 T to be $0.91\ \mathrm{m^2\,V^{-1}\,sec^{-1}}$ at room temperature and $2.3\ \mathrm{m^2\,V^{-1}\,sec^{-1}}$ at liquid nitrogen temperature; the value at liquid nitrogen temperature corresponds to that for a pyrolytic graphite heat treated at 3200° C for 1 h (PG 3200). Magnetic field dependence of Hall coefficient at liquid nitrogen temperature for this sample also agrees well with that for PG 3200. Scanning electron micrographs on the surfaces show that the present graphite films consist of grains of large crystallites, and grain size increases as the crystallinity of the material improves.

1. Introduction

A carbon film prepared from pyrolysis of the commercially available polyimide film named "Kapton" is known to be graphitized very easily [1]. The graphitization behaviour of Kapton carbon was studied by X-ray measurements in reference [1], but the authors showed only the variation of 0 0 2 diffraction profiles with heat treatment temperature (HTT). No studies have been carried out on the electronic properties of Kapton carbons as a function of HTT. In the present study, Kapton carbon was heat treated at temperatures of 2700 and 3050° C, and their structure, electrical resistivity, magnetoresistance and Hall coefficient were examined.

2. Experimental procedures

Kapton films of 50 μm in thickness manufactured by Toray Co. were used in the present study as starting materials; their chemical structure is shown in Fig. 1. They were cut into ribbons about $1 \times 30\ \mathrm{mm^2}$, and sandwiched between two gold foils further supported between two alumina plates. The supported Kapton films were heated to 800° C in flowing nitrogen in an electric furnace, with a heating rate of $400°\mathrm{C\,h^{-1}}$. Kapton carbons thus obtained were black films with metallic lustre, with reduced flexibility. Linear shrinkage after carbonization was about 20%. These ribbons were further heat treated for 1 h in a graphite furnace in pure argon at temperatures of 2700 and 3000° C. These samples were denoted as KAP 2700R and KAP 3000R, respectively. Another Kapton carbon film with an area of $30 \times 30\ \mathrm{mm^2}$ was prepared by the same way as described above, sandwiched between two polished artificial graphite plates, and heat treated in a graphite furnace to 3050° C for 30 min. The graphitized carbon film thus obtained exhibited two different coloured regions; grey regions with grains of relatively small size and black regions with grains of relatively large size. For electrical measurements, specimens were cut from these different regions and were denoted as KAP 3050F for the specimen from a grey region with fine grains and KAP 3050C for that from a black region with coarse grains.

X-ray diffraction patterns were obtained using Cu$K\alpha$ radiation for all powdered specimens, and the interlayer spacing d_{002} was determined referring to an internal standard of silicon. The diffraction profiles were corrected for the Lorents-polarization, absorption and atomic scattering factors.

For the measurements of the resistivity, magnetoresistance and Hall coefficient, rectangular specimens were cut into about $0.8 \times 5\ \mathrm{mm^2}$. Determination of

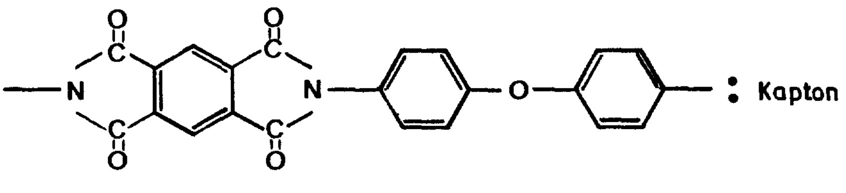

Figure 1 Chemical structure of polyimide "Kapton".

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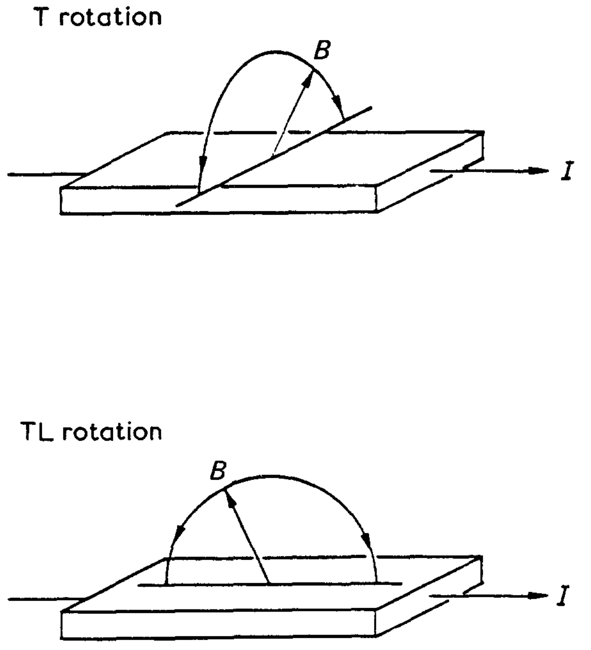

Figure 2 Magnetic field rotation schemes for the study of magnetoresistance anisotropy on graphitized Kapton carbon films.

the thickness of each specimen was carried out by observation by a scanning electron microscope (SEM). Five 25 μm diameter gold wires, two for current supply, two for voltage measurement, and one for Hall voltage measurement, were fixed to the specimen with gold paint. The Hall voltage wire was transverse to the specimen and made a pair with one of the voltage wires. For each specimen the current flowed practically along its length. The measurements were carried out at room temperature, and at liquid nitrogen temperature by direct immersion.

The magnetoresistance ($\Delta\varrho/\varrho$) is defined by

$$\Delta\varrho/\varrho = [\varrho(B) - \varrho(0)]/\varrho(0) = [\mathrm{V}(B) - \mathrm{V}(0)]/\mathrm{V}(0)$$

where $\varrho(B)$ and $\varrho(0)$ are the resistivities in magnetic field B and in zero magnetic field, and $\mathrm{V}(B)$ and $\mathrm{V}(0)$ are the voltages between voltage terminals of the specimen in magnetic field B and in zero magnetic field, respectively. The current was controlled by a Keithley 220 programmable current source and stabilized to 10 parts per million. The current density was about $40\,\mathrm{A\,cm^{-2}}$. The voltages associated with the resistivity, magnetoresistance and Hall coefficient were measured by a Keithley 181 nanovoltmeter. For the measurements of the magnetoresistance and Hall voltage, the magnetic fields of up to 1 T were applied perpendicular to the specimen surface and were measured with a Bell 640 incremental gaussmeter.

Magnetoresistance as a function of magnetic field orientation can be studied by using two magnetic field rotation schemes as shown in Fig. 2. In the first rotation scheme, denoted as T rotation, the magnetic field B is rotated so as to be always transverse to the direction of current I. In the second rotation scheme denoted as TL rotation, the magnetic field B is rotated from the direction in which B is perpendicular to the specimen surface to the direction of the current I.

After the electrical measurements, the surface structure of each specimen was observed by SEM with an acceleration voltage of 2 kV. This acceleration voltage has been shown to be particularly adopted for the observation of carbonaceous materials [2]. The surface structure of a pyrolytic graphite heat treated at 3200° C for 1 h (PG 3200), the same material used in reference [3], was observed for comparison.

3. Results and discussion

3.1. X-rays

All diffraction lines observed on all samples are very sharp. Even *h k l* lines due to three dimensional ordering of graphite layer stacking are sharp and strong,

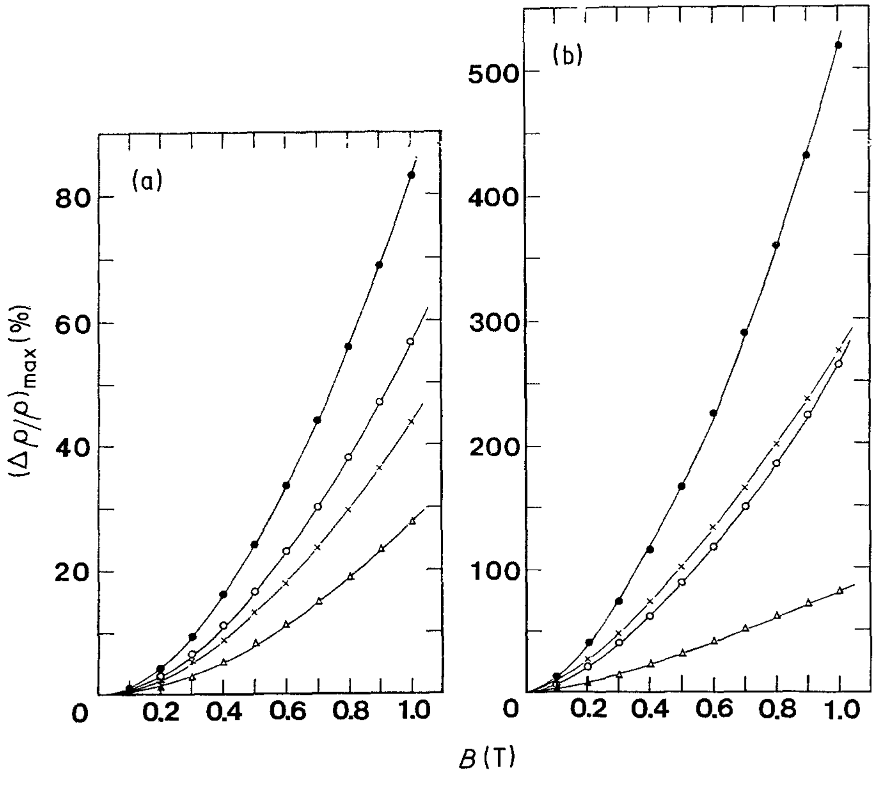

Figure 3 Maximum transverse magnetoresistance $(\Delta\varrho/\varrho)_{\max}$ for graphitized Kapton carbon films, at (a) room temperature, and at (b) liquid nitrogen temperature. (● KAP 3050C, ○ KAP 3050F, × KAP 3000R, △ KAP 2700R).

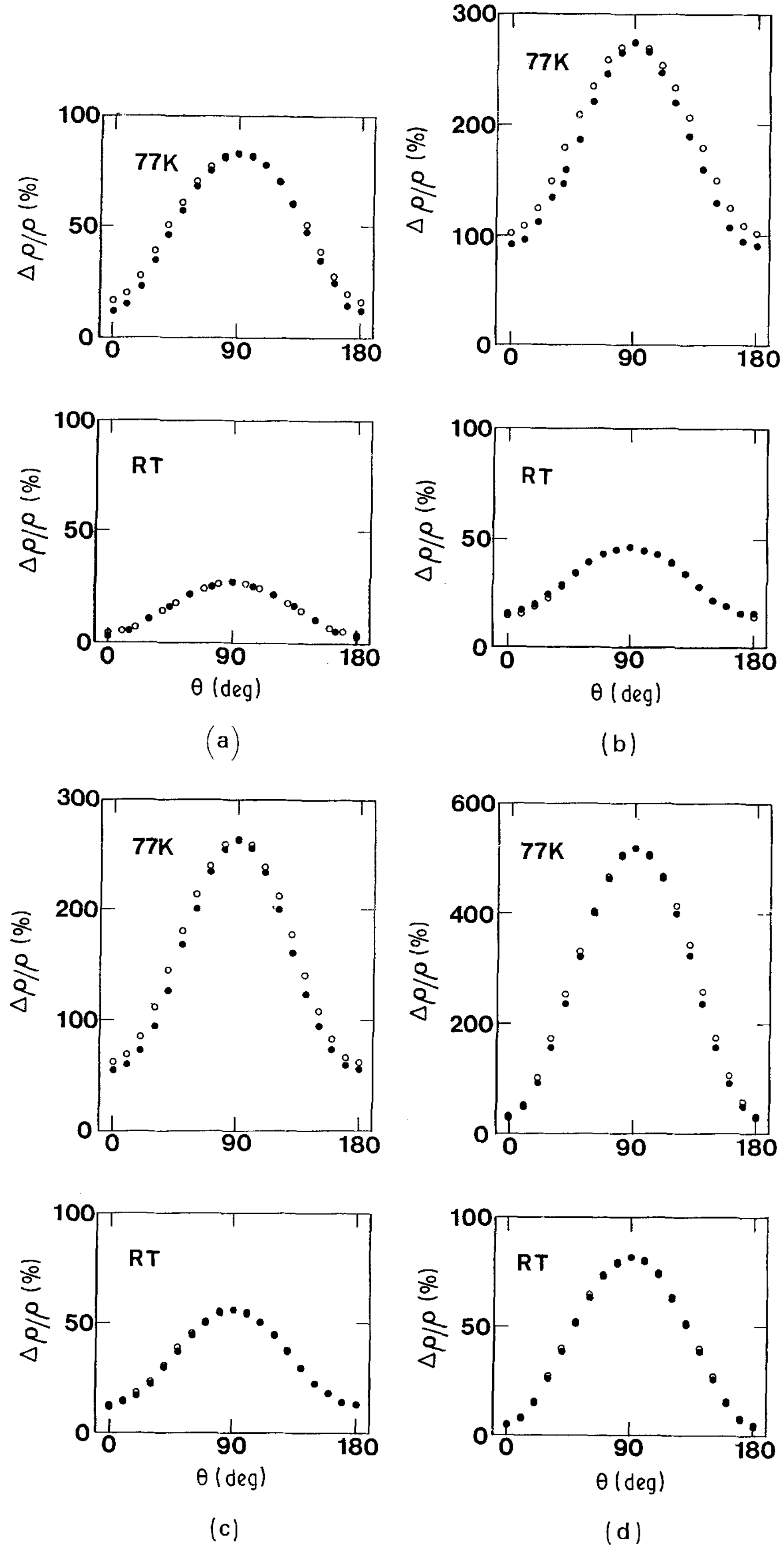

Figure 4 Dependence of the magnetoresistance on magnetic field direction in T (●) and TL (○) rotation schemes at the magnetic field of 1 T and at room temperature (RT) and liquid nitrogen temperature. (a) KAP 2700R; (b) KAP 3000R; (c) KAP 3050F; and (d) KAP 3050C.

though they are usually weak and broad on graphitized carbon materials, such as cokes. The values of d_{002} determined from 004 diffraction are 0.3356 nm for KAP 2700R, and 0.3354 nm for the samples of KAP 3000R, KAP 3050F and KAP 3050C, identical to the value for the single crystal. The Kapton carbon seems to be graphitized extremely well. The carbonized POD film was also reported to have high graphitizability [4]. The d_{002} value for KAP 2700R corresponds to that for a carbonized POD film heat treated to 2500° C. The d_{002} value of 0.3354 nm is measured for the POD carbon films heat-treated above 2800° C [4].

TABLE I Resistivities ϱ_{RT} and ϱ_{77K} at room and liquid nitrogen temperatures for the samples. Room temperature resistivity for POD carbon films are also listed for comparison. Number after POD indicate heat treatment temperature for the POD carbon films

Sample	KAP 2700R	KAP 3000R	KAP 3050F	KAP 3050C	POD 2500	POD 2800	POD 3000
ϱ_{RT} ($10^6\,\Omega$m)	1.6	1.3	0.59	0.59	1.4	1.0	0.50–0.71
ϱ_{77K} ($10^6\,\Omega$m)	2.4	1.4	0.61	0.53	–	–	–

3.2. Electrical resistivity

The values of electrical resistivities ϱ_{RT} and ϱ_{77K}, measured at room and liquid nitrogen temperatures, on the samples are listed in Table I. The room temperature resistivity for the POD carbon films heat treated at temperatures above 2500° C is also listed in Table I for comparison [5]. The values of ϱ_{RT} for KAP 3050F and KAP 3050C are close to the minimum value of ϱ_{RT} for the POD carbon films heat treated at 3000° C. A non-metallic like dependence of the resistivity on temperature is observed for the samples of KAP 2700R, KAP 3000R and KAP 3050F, while a metallic like dependence for the sample of KAP 3050C. The crystallinity of the KAP 3050C therefore seems to be quite high.

3.3. Magnetoresistance

The transverse magnetoresistance with the magnetic field applied perpendicularly to the specimen surface is the maximum transverse magnetoresistance $(\Delta\varrho/\varrho)_{max}$. Since it is much more sensitive to the improvement of structure than X-ray parameters, it is much used for structural characterization of well graphitized materials; the larger its value is, the higher the degree of graphitization, if the samples have the same preferred orientation of crystallites [6, 7]. The value of $(\Delta\varrho/\varrho)_{max}$ is plotted as a function of magnetic field for the samples in Fig. 3, and its value at the magnetic field of 1 T is listed in Table II.

The value of $(\Delta\varrho/\varrho)_{max}$ at room temperature and 1 T for the graphitized POD carbon films are reported to be 12.4% after treatment at 2500° C, 8.7% after treatment at 2800° C, and 47–66% after 3000° C treatment [5]. All these values are much lower than those of the present Kapton carbon films heat treated at corresponding temperatures.

The values of $(\Delta\varrho/\varrho)_{max}$ measured at liquid nitrogen temperature for KAP 3050C is quite large and its magnetic field dependence is similar to that for PG 3200 [3]. This fact suggests exceedingly high crystallinity of KAP 3050C, comparable to PG 3200.

The value of $(\Delta\varrho/\varrho)_{max}$ at liquid nitrogen temperature for KAP 3000R are slightly higher than those for KAP 3050F, but much lower than those for KAP 3050C, as shown in Fig. 3. This suggests that the sample of KAP 3000R partly contains large size grains, even larger than those in KAP 3050F, though the heat treatment temperature is a little lower. The coexistence of regions with different sizes of grains are verified by the measurement of magnetoresistance and also will be verified by observing the surface structure of this specimen by SEM.

The mean-square mobility $(\mu_e\mu_h)^{1/2}$ for majority carriers can be obtained from the following equation, assuming equal concentrations for electrons and holes,

$$(\mu_e\mu_h)^{1/2} = (1/B)[\Delta\varrho/\varrho)_{max}]^{1/2}$$

The value of $(\mu_e\mu_h)^{1/2}$ at 1 T can be used as a parameter for the crystallinity, though it depends on magnetic field, and values are listed for the samples in Table II. The value of $(\mu_e\mu_h)^{1/2}$ at liquid nitrogen temperature

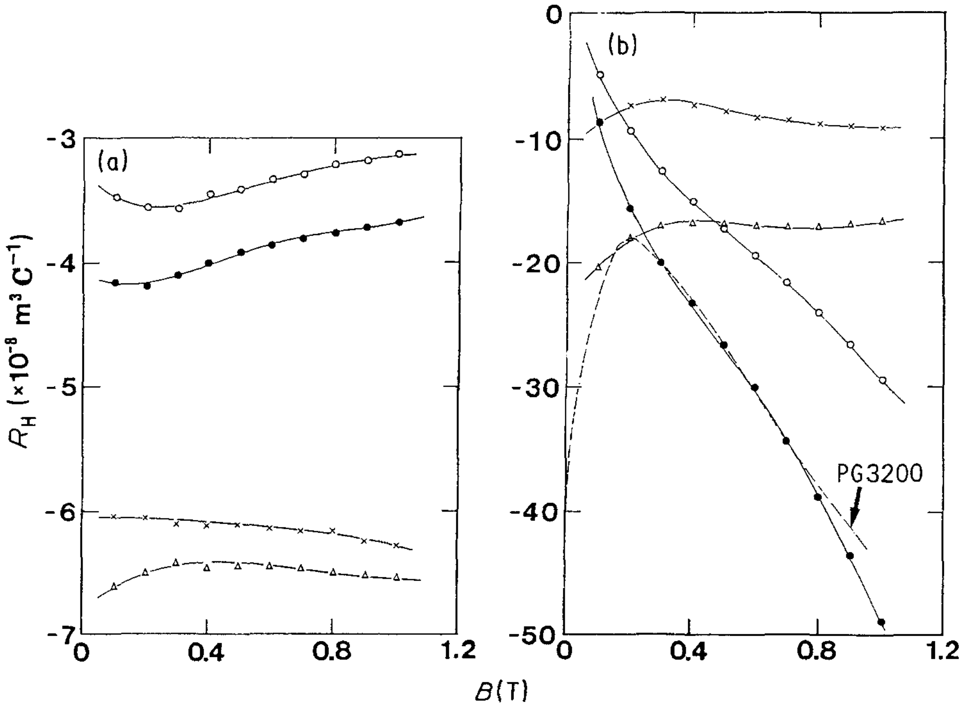

Figure 5 Hall coefficient for graphitized Kapton carbon films at (a) room temperature and (b) liquid nitrogen temperature. (● KAP 3050C, ○ KAP 3050F, × KAP 3000R, △ KAP 2700R).

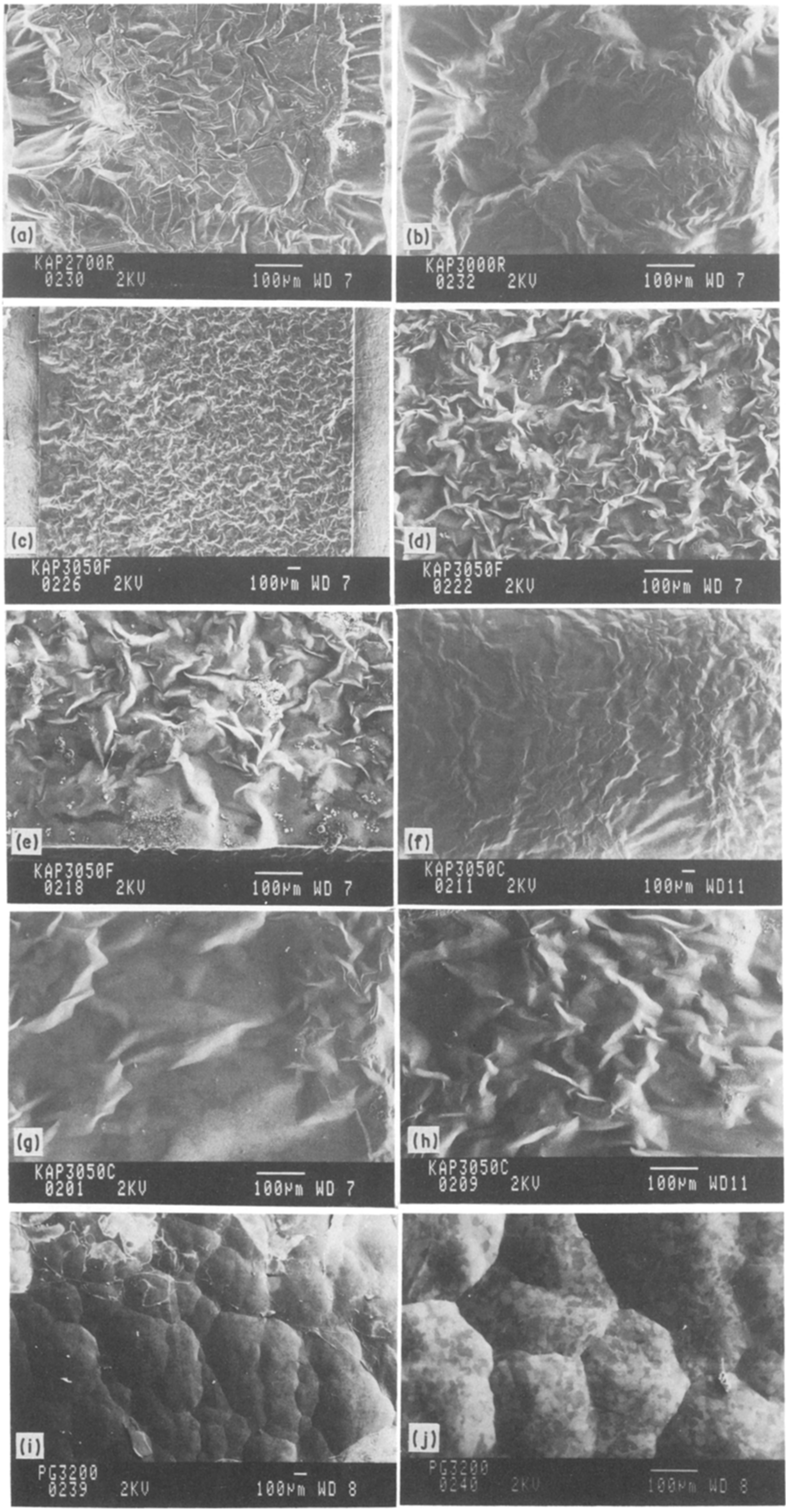

Figure 6 SEM photographs of the sample surfaces. (a) KAP 2700R; (b) KAP 3000R; (c), (d), (e) KAP 3050F; (f), (g), (h) KAP 3050C; and (i), (j) PG 3200.

TABLE II Values of the maximum transverse magnetoresistance $(\Delta\varrho/\varrho)_{\max}$, mean-square mobilities $(\mu_e\mu_h)^{1/2}$ and magnetoresistance ratios r_T and r_{TL} at room and liquid nitrogen temperatures for the samples

Sample	Temperature	$(\Delta\varrho/\varrho)_{\max}$ (%)	$(\mu_e\mu_h)^{1/2}$($\mathrm{m^2\,V^{-1}\,sec^{-1}}$)	r_T	r_{TL}
KAP 2700R	room	27.3	0.52	0.125	0.161
	liquid nitrogen	83.3	0.91	0.146	0.201
KAP 3000R	room	46.6	0.68	0.356	0.321
	liquid nitrogen	275.2	1.66	0.331	0.371
KAP 3050F	room	56.4	0.75	0.218	0.221
	liquid nitrogen	264.1	1.63	0.207	0.236
KAP 3050C	room	82.6	0.91	0.070	0.059
	liquid nitrogen	519.2	2.28	0.063	0.063

and 1 T for KAP 3050C is in exact agreement with the mean-square mobility of majority carriers at liquid nitrogen temperature for PG 3200 determined from the galvanomagnetic data ($2.2\,\mathrm{m^2\,V^{-1}\,sec^{-1}}$) [3]. The value at room temperature and 1 T for KAP 3050C is much higher than those calculated using the data in reference [4] for the 3000° C treated POD carbon films (0.69–$0.81\,\mathrm{m^2\,V^{-1}\,sec^{-1}}$).

The dependence of the magnetoresistance on magnetic field direction reflects the preferred orientation of the constituent crystallites (Fig. 2) in the sample. The results of the dependence in T and TL rotation schemes at 1T are shown in Fig. 4. The magnetoresistance ratios r_T and r_{TL} defined by the following equations can be used as parameters for the preferred orientation [7]

$$r_T = (\Delta\varrho/\varrho)_{\mathrm{Tmin}}/(\Delta\varrho/\varrho)_{\max},$$
$$r_{TL} = (\Delta\varrho/\varrho)_{\mathrm{TLmin}}/(\Delta\varrho/\varrho)_{\max}$$

and are listed for the samples in Table II. For the single crystal of graphite, both r_T and r_{TL} must be zero. For KAP 3050C these values are particularly low, suggesting preferentially parallel alignment of the basal planes of the crystallites along the sample surface.

3.4. Hall coefficient

The Hall coefficient as a function of magnetic field is plotted in Fig. 5. A negative Hall coefficient is observed for all samples at room and liquid nitrogen temperatures. Its absolute value at a constant magnetic field increases as the temperature decreases. In Fig. 5b the field dependence of the Hall coefficient at liquid nitrogen temperature for PG 3200 is drawn as a dashed curve from reference [7]. Except at low fields, Hall coefficient at liquid nitrogen temperature for KAP 3050C coincides well with that for PG 3200. The data indicate again that the crystallinity of KAP 3050C is of the order of that of PG 3200.

3.5. Surface structure

SEM photographs for the surfaces of the samples are shown in Fig. 6. The SEM photograph for PG 3200 is also shown in the figure, for comparison. All the Kapton carbon samples consists of grains of crystallites, the size of grains being distributed. On PG3200, pebble texture is observed, which comes from the original pyrolytic carbon. The average grain size in the sample increases as the crystallinity of the sample improves. As mentioned above, large grains, larger than those in KAP 3050F, are observed for KAP 3000R.The grain sizes of the KAP 3050C sample are quite large, though grains of small sizes are observed a little bit, comparable to or larger than those observed for PG 3200. The SEM photograph for this sample again suggests its high crystallinity, the degree of graphitization for this sample being almost the same as that for PG 3200, as observed for magnetoresistance and Hall coefficient.

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