CHEMISTRY LETTERS, pp. 975-978, 1990.

Highly Conductive Langmuir-Blodgett Films of Pyrolytic Polyimide

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Highly conductive Langmuir-Blodgett (LB) films were obtained by the pyrolysis of polyimide LB films at 1000°C in vacuum or under nitrogen atmosphere. The films showed the conductivity of as high as 300 S/cm, depending on the thickness of the film. The highest conductivity so far obtained was 600 S/cm. The film was stable under ambient conditions over months.

There has been growing interest in conductive Langmuir-Blodgett (LB) films as ultrathin organic conductors.[1] Most of the LB films, however, showed the conductivity less than several S/cm and the majority of the films were not stable under ambient conditions. For the application of conductive LB films to electronic devices, it is necessary to construct highly conductive LB films with stability. Recently, we have reported that LB films of tridecylmethylammonium-Au(dmit)$_2$ show the conductivity of 50 S/cm at room temperature exhibiting metallic conductivity down to around 100 K.[2,3] As an alternative way to obtain highly conductive LB films, we report here the pyrolysis of LB films of aromatic polymers. The preparation of conductive thin films by the pyrolysis of aromatic polymers has been reported by many groups.[4-6] By the use of LB method to prepare precursor films, highly ordered and ultrathin film will be obtained, which will be pyrolized at lower temperature and provide higher conductivity compared with cast films.

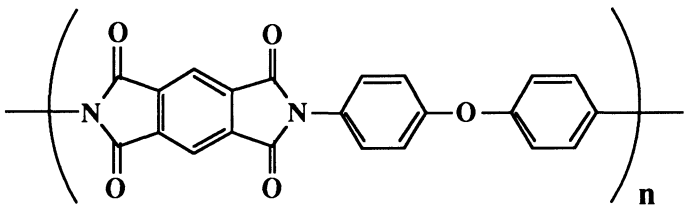

Fig. 1. Chemical structure of polyimide.

The precursor polyimide LB films were prepared according to the method of Kakimoto *et al.*[7] on the quartz substrates. The pyrolysis was achieved by heating the films in vacuum or under nitrogen atmosphere at 1000°C for 60 min. The conductivity of the films was measured perpendicular to the dipping direction by a dc 2-probe or 4-probe method using silver paste or indium as electrodes which were formed on the film surface with a gap distance of 5 mm. The thickness of the films was determined by the stylus method.[5] The tip radius was 25 μm and the stylus force was varied from 6 to 24 mgf. The thickness of the film was estimated by extrapolation.

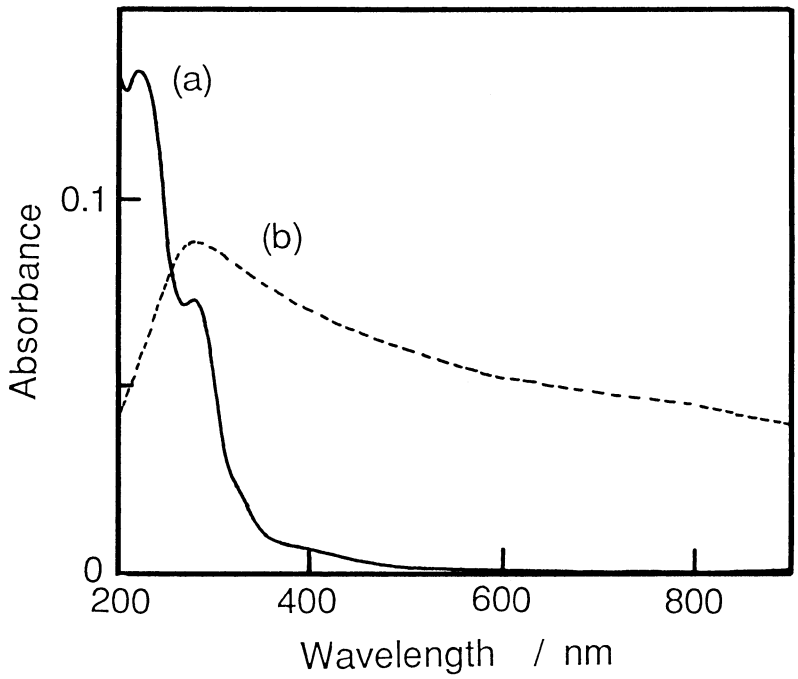

Fig. 2. Absorption spectra of 31-layered LB film before (a) and after the pyrolysis (b).

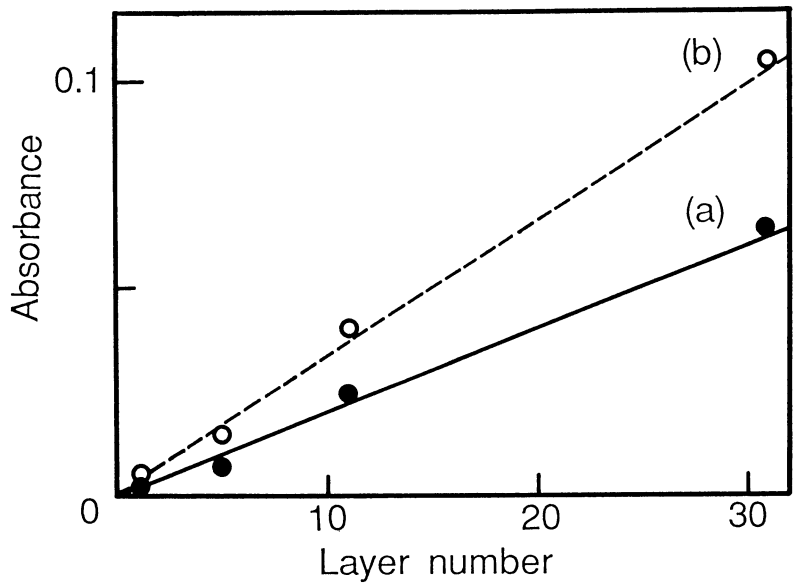

Fig. 3. Relationship between layer number and absorbance maxima of polyimide (a) and pyrolized LB film (b).

Figure 2 shows the absorption spectra of a 31-layered polyimide LB film and its pyrolyzed one. The peaks at 220 and 280 nm of polyimide disappeared after pyrolysis and a broad band with a maximum at around 270 nm spread whole region investigated, suggesting the formation of graphite-like polymer. Figure 3(a) shows the relationship between layer number and absorbance of polyimide LB film at 280 nm. The absorbance is proportional to the layer number, showing good quality of the film. The thickness of the 301-layered sample of

polyimide LB film measured by the stylus method was 970 Å (3.22 Å/layer) which agrees with that reported by Kakimoto *et al.*[7] and is comparable to that of graphite (3.35 Å/layer). The thickness of 970 Å decreased to 190 Å during pyrolysis. The commercially available polyimide film (kapton) shrank to 75 % of the original length and the weight reduced to one half its initial value by the pyrolysis under the same conditions. The thermal gravity measurement of the polyimide also showed that the mass decreased by 50 % during the heat treatment at 1000°C. Hence, the small thickness of the pyrolized LB film (0.6 Å/layer) compared with that of graphite indicates that a part of the material evaporates during the heat treatment. The amount of the material evaporated should be proportional to the thickness of the pristine film because the absorbance of LB films is proportional to the layer number after pyrolysis (Fig. 3(b)). The composition of the pyrolized LB film was estimated from elemental analysis of pyrolized polyimide which was prepared from the cast film by the same way as that of the LB film. The value thus obtained was C: 95.96 %, H: 0.43 %, and N: 3.69 %. The amount of oxygen content was below the limit of detection.

The relationship between layer number and the conductivity of pyrolized LB film is shown in Fig. 4. The 1 and 5-layered sample was insulating. The threshold point for the conductivity lies around the layer number of 31, where there is a large deviation in the conductivity ranging from 10 to 600 S/cm. The decrease in the volume of the polyimide during pyrolysis should result in the formation of island-like structure, which leads to lower conductivity in case of the sample with small layer number. The morphology of the pyrolized film was examined by scanning electron micrograph. No structure was observed which could be attributed to the formation of an island-like structure for 151-layered sample coated with gold before measurement.

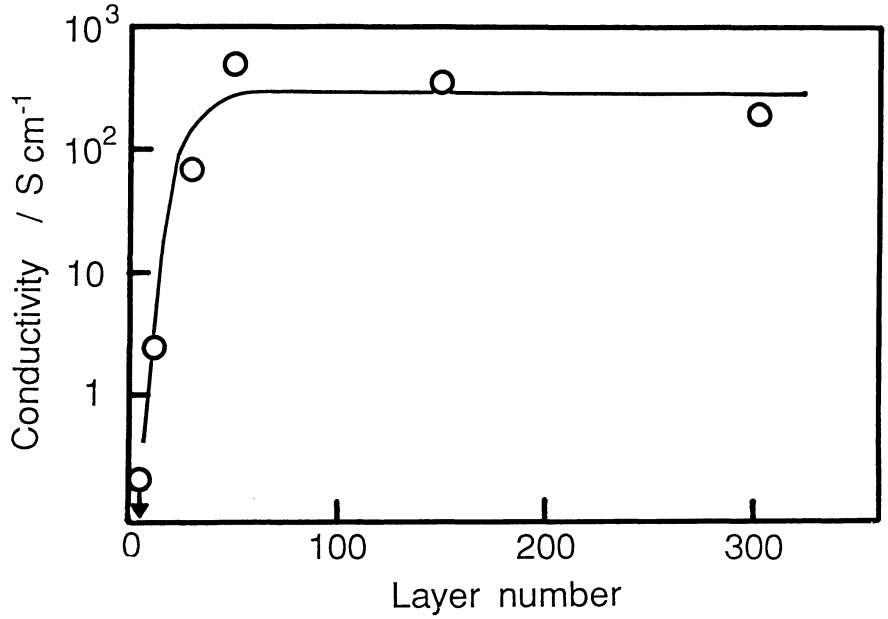

Fig. 4. Relationship between layer number and conductivity of pyrolized LB film.

The conductivity saturates at about 300 S/cm for the samples with more than 50 layers, which is almost twice as large as that of bulk pyrolytic polyimide pyrolyzed at 1000°C reported by Murakami *et al.*[5] (160 S/cm). The highest value of 600 S/cm in the present study suggests that the improvement of the experimental conditions lead to higher conductivities. Taking into account the value of 520 S/cm for pyrolytic polyimide pyrolyzed at

2500°C,[5] it is possible that the ordered structure in the pristine LB films is favorable for the network structure which is responsible for the high conductivity in the pyrolized film. The highest conductivity of the LB film, however, is lower than that of high-quality pyrographite (HOPG, 25000 S/cm) and the pyrolytic polyimide pyrolyzed at 3000°C (16000 S/cm).[6] This may be ascribed to heterographite structure of the film expected from elemental analysis described above. The film will lead to three-dimensional graphite through denitrogenation by the pyrolysis at higher temperatures. The film was stable under ambient conditions over months.

In summary, we have obtained highly conductive LB film by the pyrolysis of polyimide LB film. The conductivity of the pyrolytic polymers are improved by the cation or anion doping.[6,9] In addition, graphite exhibits the superconducting behavior by doping of alkali metal etc.[10] The studies on the improvement of conductivity of the LB films by anion or cation doping are now in progress. As the film is ultrathin and possesses the properties of pyrolyzed graphite polymer, this film will be a useful precursor of electrodes for constructing battery[11] or liquid crystal cell.[12]

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(Received March 12, 1990)