Formation of Highly-Oriented Graphite Film by Chemical Vapor Deposition Method

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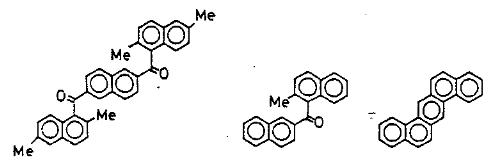
INTRODUCTION

Formation of highly-oriented thin film of graphite at low temperatures has potential for the application of graphite to electronic devices. We disclosed that crystalline graphite films can be obtained on Ni substrates kept at temperatures as low as 600℃ by using 2-methyl-1,2'naphthyl ketone as a starting material[1,2,3]. In our former studies, the orientation alignment of the film was not the aim. The thick Ni plates hindered electrical and magnetic evaluation of the film quality. For dissolving these problems at the same time, metal thin films are used as the deposition substrates in this report.

EXPERIMENTAL

Equipment used for vacuum chemical vapor deposition (CVD) is shown in Fig.1. Background pressure was 10^{-7} Torr. Temperature of the substrate was varied between 500℃ and 1000℃. Deposition rate was below 100Å/hour. Evaporation rate of the starting material was controlled to be about 1mg/20hours or less. The starting materials were o-methyl-diaryl ketones (0), (I), and dibenzanthracene (II). The deposition substrates were sapphire (A, R, C surfaces), quartz glass, metal (Ni, Co, Pt, Pd) plates, metal (Ni, Pt, Pd) thin films deposited on the sapphire, quartz glass plates and amorphous carbon (a-C) films. The metal films were formed by vacuum deposition at 10^{-6} Torr keeping the sapphire and the quartz glass plates at 350℃. The a-C films were formed on the sapphire or quartz glass plates by CVD at 1000℃ using (I) as the starting material under vacuum of 10^{-7} Torr.



(0) (I) (II)

RESULTS AND DISCUSSION

Structures of the films obtained by CVD are studied by Raman scattering spectra (Ar ion laser, 514.5nm; back scattering), X-ray diffraction analyses (CuKα line) and scanning electron microscopic observation. When the Raman spectrum of the film shows a peak at 1585cm^{-1} and the X-ray diffraction profile shows diffraction lines corresponding to (002) of graphite with the full width at half maximum (FWHM) less than 0.2°, the film is considered to be made of graphite in this study. It is apparent from Table 1 that the material (I) is suitable for the low temperature formation of graphite on the Ni plates. Table 2 indicates that the graphite thin film is obtained at such low temperature as 600℃ only when the substrate is Ni. The lowest temperatures for the graphite film formation on Pt, Co and Pd are 900℃ or 800℃. Graphite did not grow on the other metals such as Fe, Cr, W, Ti, Cu. Carbides were often found on these metals after CVD. Amorphous carbon was generated on the quartz glass.
One of the roles of Ni in the graphite film formation became apparent by

quadrupole mass spectra measured during the deposition. Only when the dehydrogenation from the starting materials was enhanced by Ni, the graphite film was formed below 700℃. When the substrate temperature was above 800℃, recrystallization of carbon into graphite from the carbon-Ni solid solution dominated the graphitization. This became apparent from an experiment in which an a-C film covered by thin Ni layer (1~2000Å) was graphitized by heat-treatment under vacuum (10^{-7} Torr) above 800℃.

For further characterization of the obtained graphite films by electrical and magnetic measurements, metal substrates must be removed or the resistance of the metal must be much greater than that of the graphite film. To realize the latter idea, Ni, Pt and Pd thin films were used as the deposition substrates. A series of experiments has shown that the metal films formed on the quartz and sapphire were transformed into metal droplets by heating. Therefore the flatness of the graphite film was quite poor. The mosaic spread obtained from the graphite (002) X-ray diffraction (Δ_{002}) took values more than several degrees. A thick Pt film, e.g. 500Å, was found to be an exception which keeps the flat surface even if it is heated up to 900℃. The graphite film grown by CVD method on the Pt film at 900℃ had the flat surface whose Δ_{002} was about 0.16°. This value is the smallest among those of synthesized graphite. However, 500Å is not thin enough for our purpose because the thickness of graphite is about several thousand Å. In order to make highly oriented graphite film using the thin metal layer, we inserted a-C layer between the metal film and the quartz glass or sapphire plates. The a-C layer avoided the transformation of the Ni film into droplets. In fact, the Δ_{002} values of the graphite film obtained using a 10Å Ni/a-C film was about 0.5°.

REFERENCES

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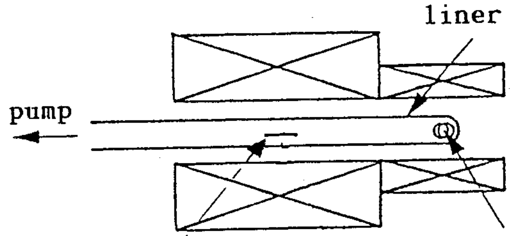

Fig.1 CVD equipment.

Table 1 Graphite film formation on Ni substrates.

	1000℃	900℃	800℃	700℃	600℃	500℃
(0)	○	○	○	×	×	×
(I)	○	○	○	○	○	—
(II)	○	○	○	△	△	—

○ crystalline graphite film; △ crystalline graphite film, small basal domain size; × disordered graphite; — no deposition

Table 2 Graphite film formation on various metal substrates.

	1000℃	900℃	800℃	700℃	600℃	500℃
Ni	○	○	○	○	○	—
Pt	○	○	—			
Pd	○	○	○	—		
Co	○	○	○	—		
quartz glass	×	×	×	—		

○ crystalline graphite film; × disordered graphite; — no deposition