Journal of Korean Institute of surface Engineering
Vol. 29, No. 5, Oct., 1996

NITROGEN DOPED DIAMOND LIKE CARBON FILM SYNTHESIZED BY MICROWAVE PLASMA CVD

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ABSTRACT

Diamond Like Carbon film is amorphous film which is considered to consist of three coordinate graphite structure and tetrahedron coordinate diamond structure.Its hardness, thermal conductivity and chemical stability are nearly to one of diamond. It is well known to become semi-conductor by doping of inpurity.In this study Diamond Like Carbon film was synthesized by Microwave Plasma CVD in the gas mixture of hydrogen-methan-nitrogen and doped of nitrogen on the single-crystal silicon or silica glass. The temperature of substrate and nitrogen concentration in the gas mixture had an effect on the bonding state, structural properties and conduction mechanism. The surface morphology was observed by Scanning Electron Microscope. The strucure was analyzed by laser Raman spectrometry. The bonding state was evaluated by electron spectroscopy.

Diamond Like Carbon film synthesized was amorphous carbon containing the sp^2 and sp^3 carbon cluster. The number of sp^2 bonding increased as nitrogen concentration increased from 0 to 40 vol% in the feed gas at 1233K substrate temperature and at 7.4×10^3 Pa. Increase of nitrogen concentration made Diamond Like Carbon to be amorphous and the doze of nitragen could be controlled by nitrogen concentration of feed gas.

INTRODUCTION

An insulator like diamond including impurity or lattice defect tends to behave semiconductor. Diamond having wide bandgap and as high career mobility as silicon and germanium is expecting to use as semiconductor material[1]. Diamond thin film consists of micoro crystals and nitrogen doped diamond becomes n-type semiconductor[2-4]. In this case its resistivity is too high to be for practical use.

Diamond like carbon is amorphous and its hardness, thermal conductivity and chemical stability are nearly to one of diamond[5-7]. Cutting tools, protective film on hard-disk, heat-sink for VLSI and diamond semiconductor under high temperature are practical applications for DLC.

In this study Diamond like carbon film was synthesized by Microwave Plasma CVD in the gas mixture of hydrogen-methan-nitrogen and doped of nitrogen to be amorphous and semiconductor[8].

EXPERIMENTAL PROCEDURE

Pre-treatment of substrate

Syngle-crystal Silecon size of 10×10×0.5 mm and quartz glass size of 10×10×1.1mm were used as substrate. Substarate surface was scratched by 0.25μm diamond paste and rinced using ultra sonic cleaning in aceton. Density of nucleation will increase to scratch substrate in diamond synthesis.

Synthesis of DLC films by Microwave Plasma CVD

Schematic apparatus of microwave plasma CVD is shown in Fig. 1. Reaction chamber was evacuated to 1.33 Pa by rotary pump and hydrogen-methan-nitrogen gas was introduced into the chamber to be at 9.33×10^3 Pa. Plasma was excited near the substrate by microwave. The mixture gases were reacted in plasma and DLC film was systhesized on the substrate. Substrate temperature was measured by pyrometer (CHINO : model IR-U). The conditions for synthesis of DLC films are shown in Table 1.

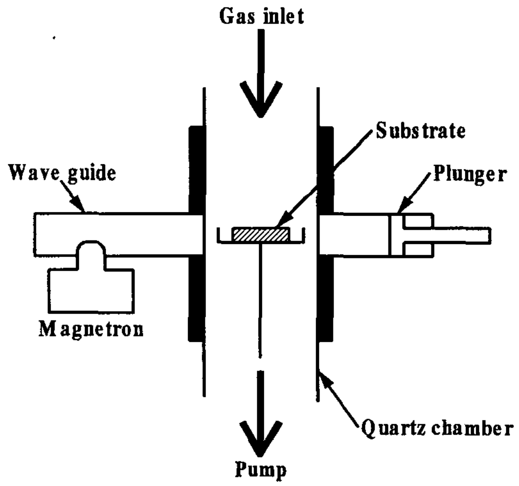

Fig. 1 Schematic apparatus of microwave plasma CVD

Table. 1 Conditions for synthesis of DLC films by microwave plasma CVD

Main	H_2+5 vol% CH_4
N_2 concentration/vol%	0, 5, 10, 20, 30 and 40
Substrate temperature/K	1123, 1183, 1233, 1303
Chamber pressure/Pa	9.33×10^3
Reaction time/s	1440
Microwave power/W	200-400

Evaluation

The strucure was analyzed by laser Raman spectrometry : Nihon-bunkoh, NR-1100(Ar-ion laser, l=5.145nm). The bonding stete was evaluated by electron spectroscopy : Shimazu -seisakuksyo, ESCA 750. The surface morphology was observed by Scanning Electron Microscope : Nihon-denshi : JSM 5200. The electromotive force characteristic of synthesized film for temperatue between 173 to 373K was measured by cryostat.

RESULT AND DISCUSSION

Effect of nitrogen concentration

Fig. 2 shows Raman spectres of carbon films synthesized at nitrogen concentration of 0, 5, 10, 20, 30 and 40% at 1233K. All lines presented two broad Raman bands with center of 1550 and 1360cm^{-1}. Generally Raman bands with center of 1550cm^{-1} and 1360cm^{-1} are considerd to be related to sp^2 and sp^3 cruster respectively. The former band is called G-band and the latter is called D-band. That is

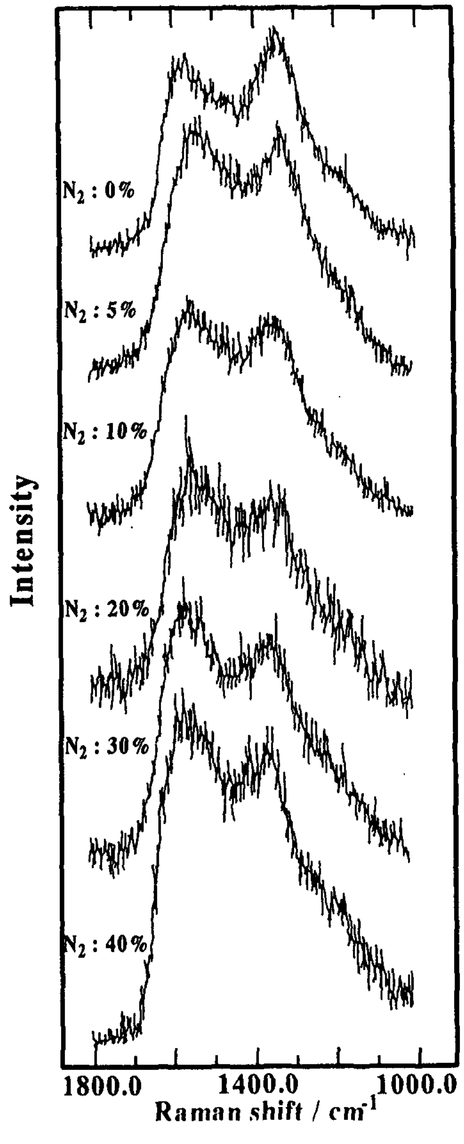

Fig. 2. N_2 concentration dependence on Raman spectra for carbon films synthesized at 1233K.

to say, the synthesized films were amorphous carbon films with diamond combination, sp^3 and graphite combination, sp^2. The D-band peak tended to be smaller than G-band peak with increasing of nitrogen concentration, i.e. xxxsp^2 combination increased with increasing of nitrogen concentration.

Fig. 3 shows ESCA spectres of carbon films synthesized at same condition. The C1s main peak of 0, 5, 10, 20, 30 and 40 nitrogen % was at 284.4, 285.2, 285.0, 285.5, 286.0 and 286.0 eV respectively and the main peak was shifted to high energy. A peak related to sp^2 combination became weak relatively because acitivated nitrogen generated in plasma physical and chemical-etched weak sp^2 combinated carbon selectively. C1s peak of 30 and 40 nitrogen % had strong 287 eV peak related to sp^3 combination.

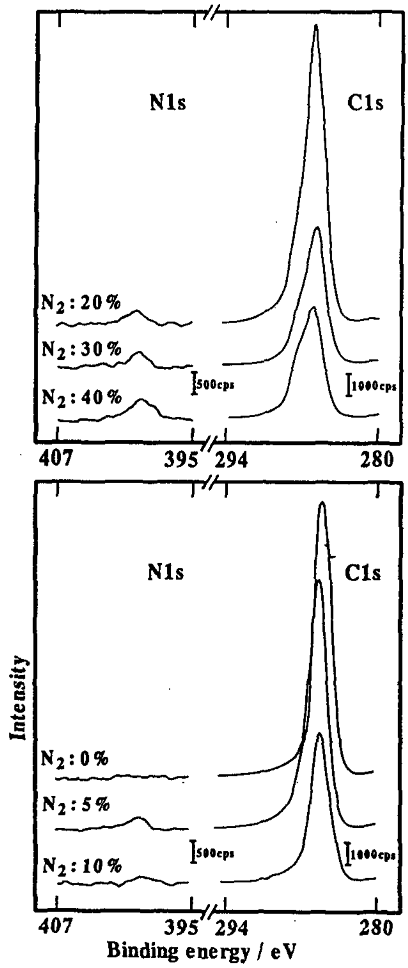

Fig. 3 N_2 concentration dependence on ESCA spectra for carbon films synthesized at 1233K

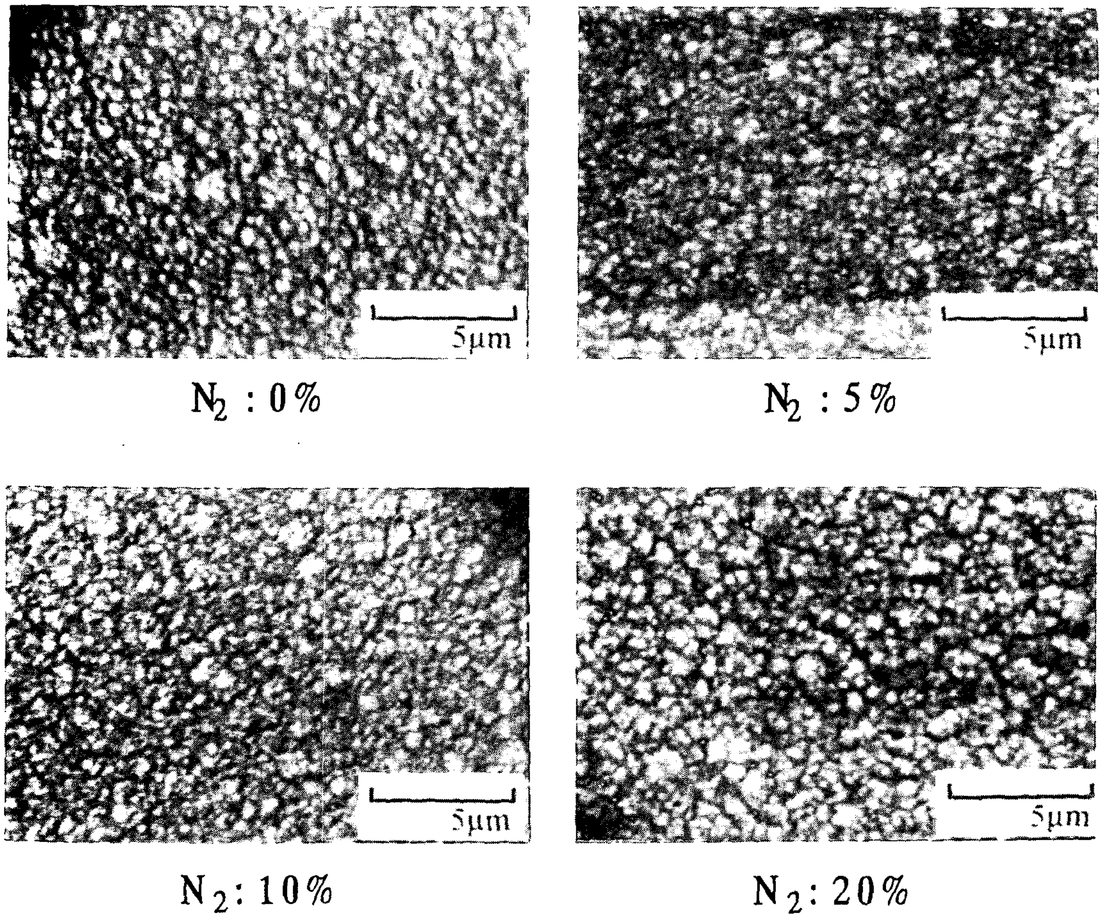

Fig 4. SEM micrographs of carbon film synthesized at 1233K with defferent N_2 concentration

The film growth rate was slower with increase of nitrogen concentration and at 40 nitrogen % the synthesized products were particles on the substrate sparsely. Fig. 4 shows surface SEM images of carbon films at 0, 5, 10 and 20 nitrogen %. All photos presented the film was growthed uniformly but the size of ball-like amorphous carbon became bigger with nitrogen concentration.

Effect of substrate temperature

Fig. 5 shows Raman spectra of carbon films sysnthesized at 1123K, 1183K, 1233K and 1303K in gases of 10 nitrogen %. The line of film synthesized at 1123K presented Raman line near 1580cm^{-1} and 1200cm^{-1} and raman band with center of 1360cm^{-1}. This means that the synthesized film include graphite. The line of film synthesized at 1183K presented Raman band with centers of 1550cm^{-1} and 1360cm^{-1}. The line of film synthesized at 1233K presented sameRaman bands and the fomer is a littele higher than the latter. In the line of film synthesized at 1303K the latter band of 1360cm^{-1} is a littel higher than the former. This means that the film synthesized at 1303K presented of Raman band of 1360cm^{-1} related to sp^3 co-

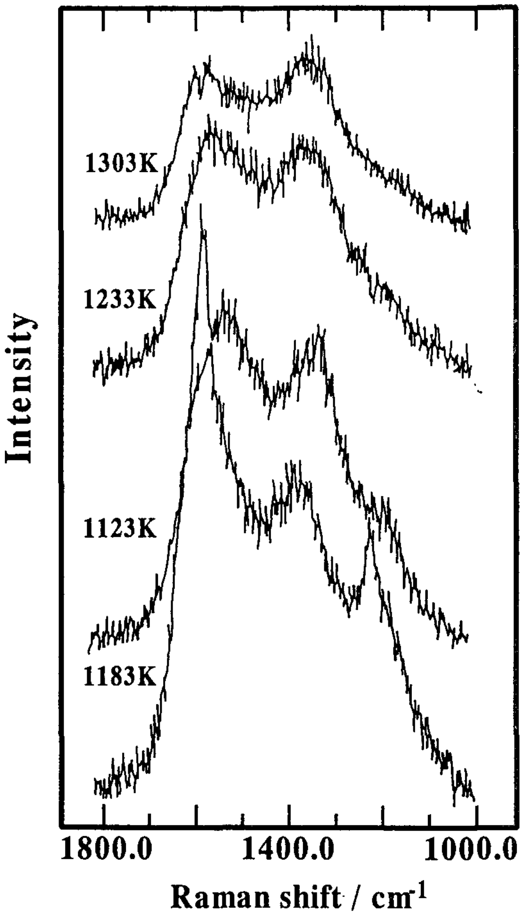

Fig. 5. Substrate temperature dependence on Raman spectra for carbon films synthesized in 10% N_2-H_2-CH_4 gasses.

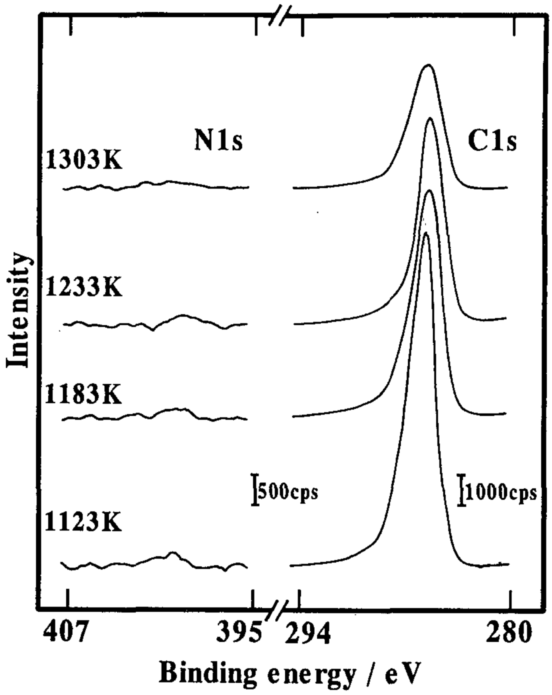

Fig. 6 Substrate temperature dependence on ESCA spectra for carbon films synthesizedin 10 %N_2-H_2-CH_4 gases.

ordinate may consist of crystal diamond and the film synthesized at 1233K presented of raman band of 1550cm^{-1} related to sp^2 coordinate may consist of amorphous carbon.

Fig. 6 shows ESCA spectres at same condition. All peaks had same C1s main peak position and width of peak hem. The peak strength related C-Hx combination at 285.5 eV of film sysnthesized at lower temperature became higher, i.e. such afilm had many hydrogen bonds.

Fig. 7 shows surface SEM images of carbon films at same condition. The photo of film synthesized at 1123K presented non-crystal particles and the one of film synthesized at 1303K presented crystalline ball-like carbon.

Electoricmotive force characteristic

Fig. 8 shows temperature characteristic of electricmotive force for N-doped DLC film and undoped DLC film. As shown in figure Au and Al film were evapolated on both sides of DLC film. The electoricmotiv force was measured between 173 to 373K in 1.33 Pa. The electromotive force of N-doped DLC film was much bigger than the one of undoped DLC film. N-doping might make DLC film to be amorphous and the number of carrier in DLC film increased.

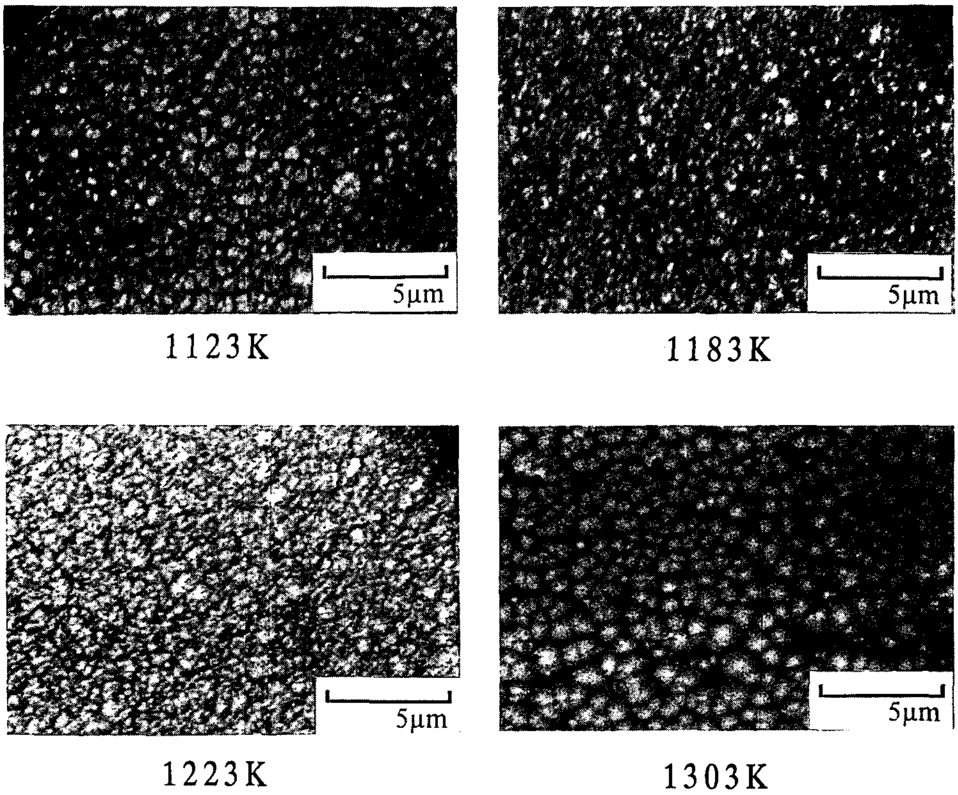

Fig. 7 SEM mixrographs of carbon films synthesized in 10% N_2-H_2-CH_4 gases with different substrate temperature.

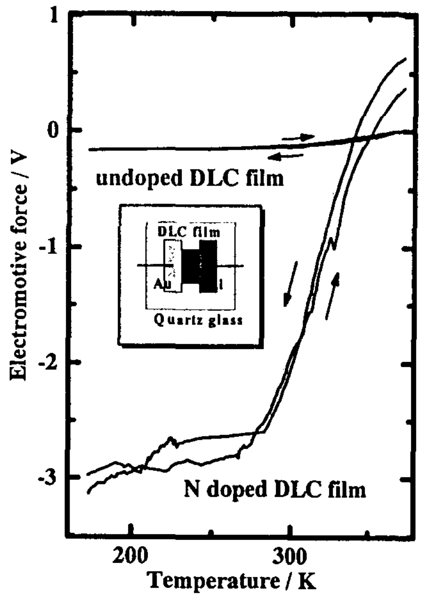

Fig. 8 Temperature characteristic of electromotive forcd for DLC film.

CONCLUSIONS

Diamond like carbon film was syngthesized by microwave plasma CVD. The film was analyzed by Raman spectrometry, ESCA and observed by SEM. The electromotive force was measured between 173 to 373K. The following results were given.'

1) Synthesized film was amorphous carbon containing the sp^2 and sp^3 carbon cluster.

2) The number of sp^2 bonding increased as nitrogen concentration increased from 0 to 40 vol% in the mixture gases at 1233K substrate temperature in 9.33 × 103 Pa.

3) Increase of nitrogen concentration made diamond like carbon to be amorphous and the doze of nitragen could be controlled

by nitrogen concentration of mixture gases.

4) N-doped DLC film presented large electromotive force between 173 to 373K.

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