

# Diamond-like carbon films prepared from $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$ mixed gas using a microwave plasma

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Diamond-like carbon films were synthesized on polished silicon substrates from  $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$  mixed gas using a microwave plasma technique. The film properties were studied. Their growth rate was several times as fast as that for  $\text{CH}_4\text{-H}_2$  mixed gas under the same experimental conditions. The films have a large Vickers hardness (5000 to 6000  $\text{kg mm}^{-2}$ ), high electrical resistivity ( $10^{12}$  to  $10^{13}$   $\Omega \text{ cm}$ ) and good optical transparency, especially in the infrared region. Low hydrogen and oxygen contents in the films were detected by secondary ion mass spectroscopy.

## 1. Introduction

In recent years, many studies on diamond or diamond-like amorphous carbon synthesis from the gas phase have been made. The interest these films have attracted is due to their many potential applications, including use as a heat sink substrate for semiconductor devices, an optical coating material for optical elements and a hard material for machine tools.

Nyaish and Holland [1] synthesized amorphous carbon films from isopropane on a water-cooled polycarbonate substrate using a radio-frequency (r.f.) plasma. They reported potential optical and ophthalmic uses for the films obtained. Dischler *et al.* [2] also obtained amorphous carbon films by r.f. plasma deposition from benzene; these had good optical transparency in the infrared region.

However, the films in both studies had lower density, mechanical hardness and electrical resistivity

than diamond-like carbon films. Kamo *et al.* [3] prepared diamond or diamond-like carbon thin films from  $\text{CH}_4\text{H}_2$  mixed gas using a microwave plasma. These films had both high hardness and electrical resistivity. At a recent symposium [4], we reported that the growth rate of diamond or diamond-like carbon particles was promoted by water addition to the  $\text{CH}_4\text{-H}_2$  mixed gas plasma.

In the present paper, diamond-like carbon thin films were synthesized from  $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$  mixed gas using a microwave plasma. Physical and chemical properties of these films were examined.

## 2. Experimental apparatus and methods

The microwave deposition apparatus is shown in Fig. 1. It was similar to that used by Kamo *et al.* [3] except for the section on water addition to the  $\text{CH}_4\text{-H}_2$  mixed gas. A single-crystal silicon wafer (20 mm ×

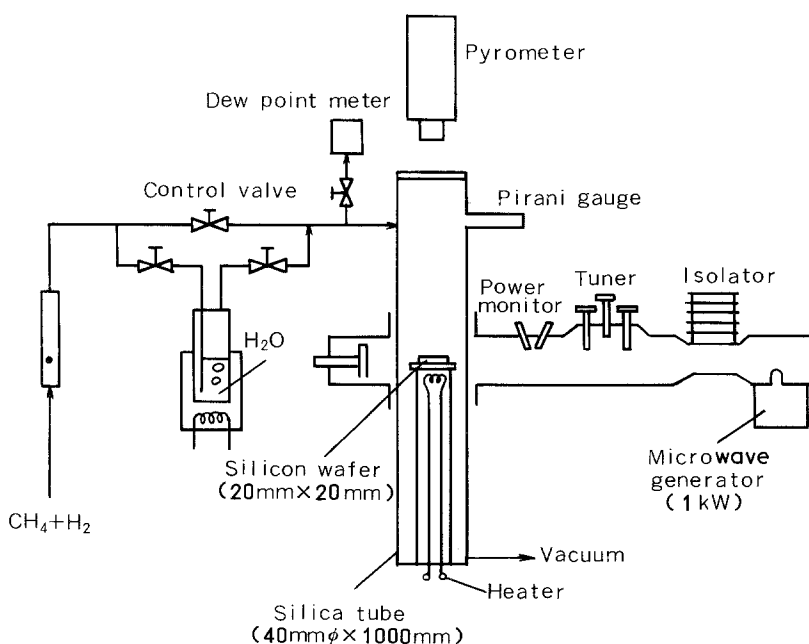


Figure 1 Experimental apparatus.

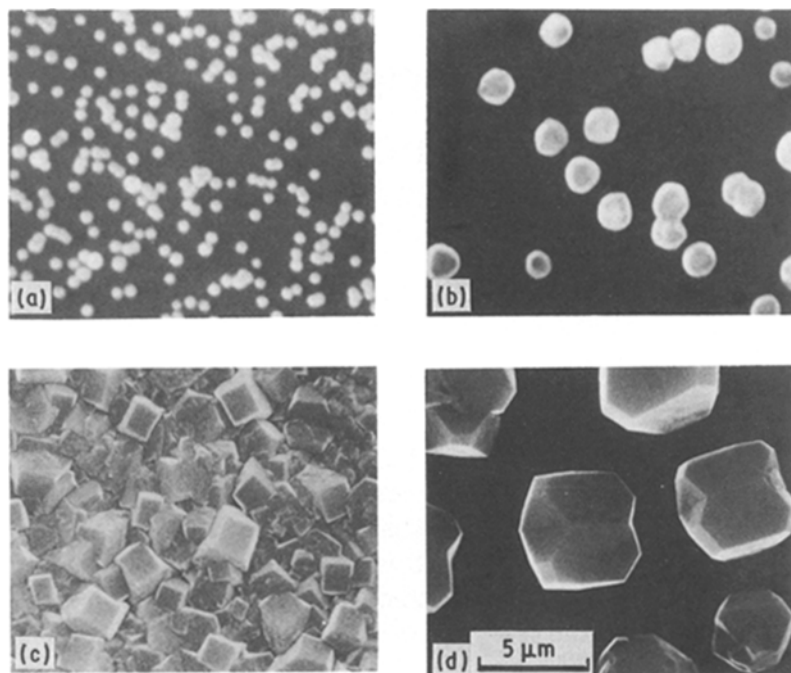


Figure 2 SEM of deposits on polished and non-polished substrates. Formation conditions: 3 vol %  $\text{CH}_4$ ,  $750^\circ\text{C}$ , 2600 Pa, and power 1 kW. (a) Polished substrate, 15 min reaction; (b) non-polished, 15 min; (c) Polished, 2 h; (d) non-polished, 2 h.

20 mm), polished with diamond paste (particle size  $1\ \mu\text{m}$ ), was used as substrate. The substrate was washed with distilled water for half an hour in an ultrasonic cleaner and then placed on a porous silicon plate in a silica glass tube (inner diameter 40 mm, length 1 m). After evacuation to 10 Pa by a rotary vacuum pump, a continuous flow of  $\text{CH}_4 + \text{H}_2$  mixed gas was introduced into the tube through a water bubbling bottle.

Microwaves (2.45 GHz) were supplied to the tube through an isolator, tuner and power monitor to generate a plasma of the synthesis gas. The substrate was heated up to a temperature of several hundred degrees Celsius by the microwave power and if necessary, a heater. The temperature and pressure were measured by a pyrometer and Pirani gauge, respectively. The film-like deposits on the silicon substrate were observed by scanning electron microscopy (SEM) and identified by low-angle X-ray diffraction analysis and Raman spectroscopy. Optical absorption of the films was measured in the infrared (IR) and ultraviolet (UV) regions. Film composition was analysed by secondary ion mass spectroscopy (SIMS).

Other properties of the films such as hardness, resistivity, roughness and stress were also measured.

The experimental conditions are summarized in Table I.

### 3. Results and discussion

Film-like diamond has been grown on scratched or polished substrates [3]. In the present experimental work, the silicon wafer was polished with diamond paste for 10 min. SEM of deposits on polished and non-polished (mirror-finished) silicon wafers is shown in Fig. 2. Many small deposits are observed on the former substrate after 15 min. Each deposit continues to grow, making contact with nearby ones until a film-like deposit is formed after 2 h. On the other hand, in the case of the mirror-finished silicon wafer, a small number of deposits is seen after 15 min, but no film-like deposit is obtained. The polishing leads to an increase in the active site density for diamond crystallization.

The properties of film-like deposits depend on the experimental conditions. SEM of two typical film-like

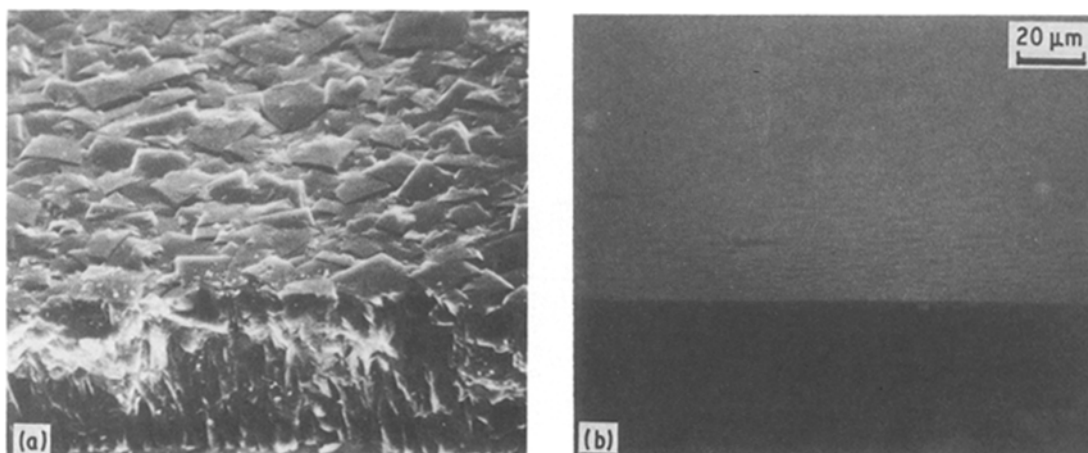


Figure 3 SEM of typical film-like deposits. (a) Film A: 3 vol %  $\text{CH}_4$ ,  $750^\circ\text{C}$ , 2600 Pa, 1 kW, 50 h. (b) Film B: 10 vol %  $\text{CH}_4$ ,  $550^\circ\text{C}$ , 2600 Pa, 1 kW, 8 h.

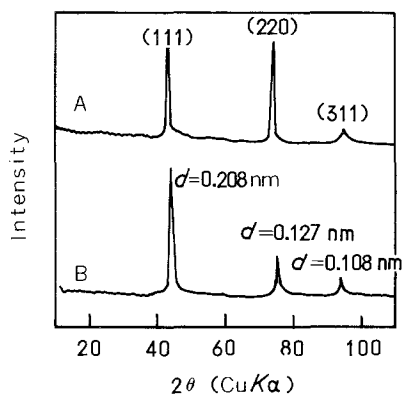


Figure 4 X-ray diffraction patterns of Films A and B (X-ray incident angle  $2^\circ$ ).

deposits is shown in Fig. 3. These are cross-sectional views of the films. A bumpy film (Fig. 3a) is formed under the rather low  $\text{CH}_4$  concentration of 3 vol % and higher substrate temperature of  $750^\circ\text{C}$ . The smooth sheet-like film (Fig. 3b) is obtained under the higher  $\text{CH}_4$  concentration of 10 vol % and lower substrate temperature of  $550^\circ\text{C}$ . Low-angle X-ray diffraction patterns of these films are shown in Fig. 4. Three prominent diffraction peaks are observed in both films at interlayer spacings ( $d$ -values) of 0.208, 0.127 and 0.108 nm which correspond to (1 1 1), (2 2 0) and (3 1 1) planes of diamond. However, the diffraction intensity ratios of the (1 1 1), (2 2 0) and (3 1 1) planes differs between the two films; for Film A, 96 : 100 : 14; and for Film B, 100 : 27 : 14. The diffraction intensity ratio of film B is in good agreement with that for diamond powder. Crystals of Film A orient to the (2 2 0) plane, but no orientation occurs in Film B.

Fig. 5 shows Raman spectra of these films. A sharp peak at  $1332\text{cm}^{-1}$  and a broad peak at about  $1500\text{cm}^{-1}$  are observed in Film A. The peak at  $1332\text{cm}^{-1}$  is found for diamond crystal [3]. Assignment of the peak at  $1500\text{cm}^{-1}$  is not clear, but a very similar peak has been observed in the Raman spectra of diamond particles containing amorphous carbon, prepared from  $\text{CH}_4\text{-H}_2$  plasma [3]. For Film B, two broad peaks at 1332 and  $1500\text{cm}^{-1}$  are observed. The results of X-ray diffraction and Raman spectroscopy indicate that these films are composed of diamond and amorphous carbon. The diamond content must be greater in Film A than in Film B.

Previously, we found that the growth rate of diamond particles was promoted by water addition to  $\text{CH}_4\text{-H}_2$  feed gas [4]. Then growth rate of film-like diamond from  $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$  mixed gas is therefore examined here. The effect of methane concentration on the film-like diamond growth rate is evaluated while changing the methane concentration from 1 to 10 vol % under a constant substrate temperature of  $750^\circ\text{C}$ , pressure of

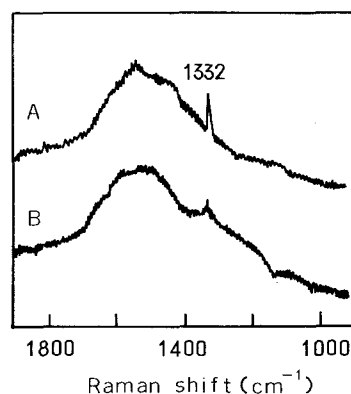


Figure 5 Raman spectra of Films A and B.

$2600\text{Pa}$  and water content of 2 vol %. In Fig. 6, growth rates of the film-like deposits from the  $\text{CH}_4\text{-H}_2$  and  $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$  systems are plotted. The growth rate increases almost linearly with increasing methane concentration in both systems. The growth rate of the  $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$  system is several times as fast as that of the  $\text{CH}_4\text{-H}_2$  system. The increased growth rate on water addition is considered to be due to the promotion of methane decomposition. Acceleration of the methane decomposition reaction has been verified by plasma emission spectra analysis of the  $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$  and  $\text{CH}_4\text{-H}_2$  systems [4]. In the present paper, the effect of water addition on by-product graphite removal reactions is tested. In the experiment, the small microwave plasma deposition apparatus (80 W) described in by Saito *et al.* [5] was utilized. Pyrolytic graphite and synthetic diamond particles of the same size ( $1.5\text{mm} \times 1.5\text{mm} \times 1.5\text{mm}$ ) were used as starting materials. As shown in Fig. 7, the residual weight of diamond particles after a 6 h reaction in  $\text{H}_2$  or  $\text{H}_2 + \text{H}_2\text{O}$  plasma is very small. It is clear that diamond has a very good resistivity to plasma etching.

On the other hand, graphite is easily etched by a hydrogen plasma and the etching rate is doubled by the addition of water at a concentration of 2 vol %. Water addition seems to ensure that graphite-free films are prepared from the higher  $\text{CH}_4$  concentration (10 vol %) feed gas, unlike the  $\text{CH}_4\text{-H}_2$  system in which suitable  $\text{CH}_4$  concentrations are much lower, 0.5 to 3 vol %.

The effect of microwave power on film-like diamond growth rate is shown in Fig. 8. The growth rate

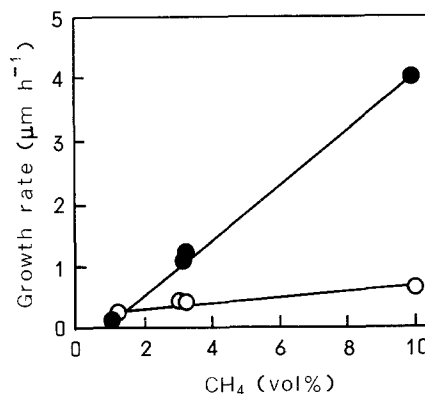


Figure 6 Effect of  $\text{CH}_4$  concentration on growth rate. Formation conditions:  $750^\circ\text{C}$ ,  $2600\text{Pa}$ ,  $0.5\text{kW}$ . (●)  $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$ , (○)  $\text{CH}_4\text{-H}_2$ .

TABLE I Experimental conditions

|  |                      |
|--|----------------------|
| Substrate                                  | Si (1 1 1)           |
| Substrate temperature ( $^\circ\text{C}$ ) | 550 to 750           |
| Pressure (Pa)                              | 2660                 |
| Microwave power (kW)                       | 0.3 to 1.0           |
| Feed gas (vol %)                           | $\text{CH}_4$        |
|  | $\text{H}_2$         |
|  | $\text{H}_2\text{O}$ |
|  | 1 to 10              |
|  | 97 to 88             |
|  | 2                    |

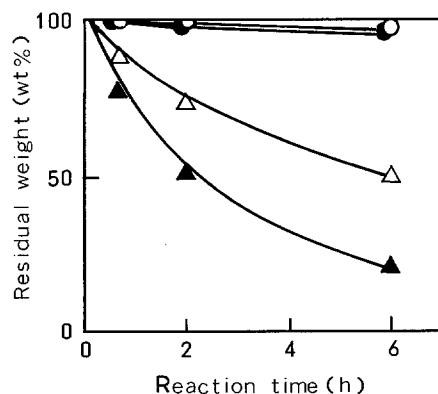


Figure 7 Effect of H<sub>2</sub>O addition on graphite removal reaction. Formation conditions: 750°C, 260 Pa, 80 W. (●) Diamond, H<sub>2</sub> + H<sub>2</sub>O plasma; (○) diamond, H<sub>2</sub> plasma; (▲) graphite, H<sub>2</sub> + H<sub>2</sub>O plasma; (Δ) graphite, H<sub>2</sub> plasma.

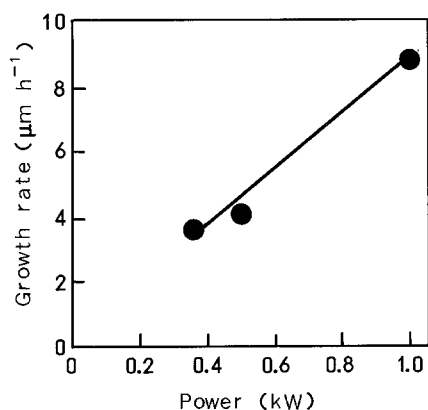


Figure 8 Effect of microwave power on growth rate. Formation conditions: 750°C, 2600 Pa.

increases with increasing microwave power. This is easily explained by increases of the incident microwave power promoting the decomposition reaction of methane as described by Kawahara [6].

IR transmittance was measured using two films (A' and B', about 4 μm thickness) prepared under the same conditions as Films A and B, respectively. As shown in Fig. 9, no absorption peak is observed in film A', but two very weak absorption peaks at 2920 cm<sup>-1</sup> (No. 1) and at 1550 cm<sup>-1</sup> (No. 2) are detected in Film B'.

The No. 1 peak is assigned to stretching of a monohydride (CH) bonded sp<sup>3</sup> type carbon and the No. 2 peak may be assigned to C=C stretching bands. No OH (3500 to 3600 cm<sup>-1</sup>) or CO (1600 to 1900 cm<sup>-1</sup>) stretching bands are detected in either film. These results show that the films deposited under CH<sub>4</sub>-H<sub>2</sub>-H<sub>2</sub>O plasma have good IR transparency.

The UV absorption spectrum was measured using thin, free-standing film prepared by dissolving the

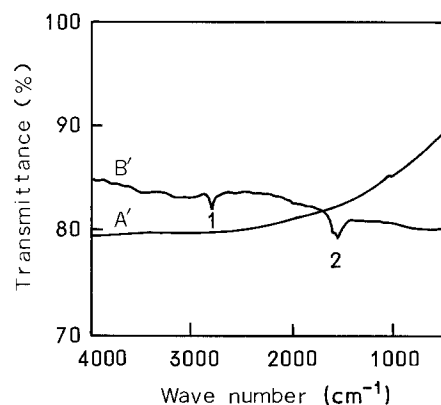


Figure 9 IR spectra of Films A' and B' (thickness 4 μm) prepared under the same conditions as Films A and B, respectively.

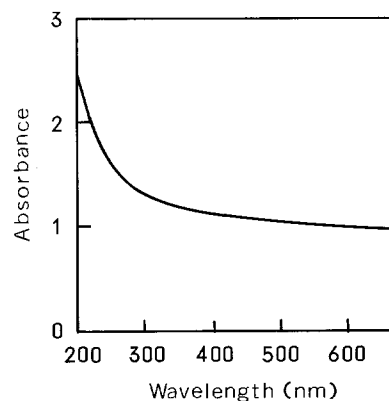


Figure 10 UV spectrum of a film (thickness 8 μm) prepared under the same conditions as Film A.

silicon substrate in a mixture of hydrofluoric acid and nitric acid. A film with a thickness of about 8 μm was synthesized under the same conditions as Film A. Its UV spectrum is shown in Fig. 10. The absorbance is about 1 at wavelengths of 300 to 600 nm, which corresponds to 10% transmittance. The calculated transmittance value for a 1 μm thick sample using Lambert's law is 75%.

Fig. 11 shows the results of SIMS of Film A. H<sup>+</sup>, C<sup>+</sup>, CH<sub>x</sub><sup>+</sup> (x = 1 - 3), CH<sub>4</sub><sup>+</sup> or O<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, C<sub>2</sub>H<sub>x</sub><sup>+</sup> (x = 1 - 3), C<sub>2</sub>H<sub>4</sub><sup>+</sup> or CO<sup>+</sup> and the like are detected in spite of the absence of CH, OH and CO stretching bands in the IR spectra of Film A. The intensity of these fragmental ions decreased after Ar<sup>+</sup> sputtering for 5 h. The results suggest that hydrogen and oxygen contents are high in the surface region.

Other properties of the films are summarized in Table II. The densities of Films A and B were measured with an areometer using diiodide methane and are 3.4 and 3.3, respectively. These are higher than for graphite

TABLE II Physical properties of the films

| Property                                | Sample           |                       |                                      |
|---|------------------|-----------------------|--------------------------------------|
|   | Film A           | Film B                | Natural diamond                      |
| Density (g cm <sup>-3</sup> )           | 3.4              | 3.3                   | 3.51                                 |
| Vickers hardness (kg mm <sup>-2</sup> ) | 6000             | 5000                  | 10 000                               |
| Resistivity (Ω cm)                      | 10 <sup>13</sup> | 10 <sup>12</sup>      | 10 <sup>14</sup> to 10 <sup>16</sup> |
| Roughness (μm)                          | 0.5              | 0.02                  | -                                    |
| Stress (Nm <sup>-2</sup> )              | -                | 1.5 × 10 <sup>7</sup> | -                                    |

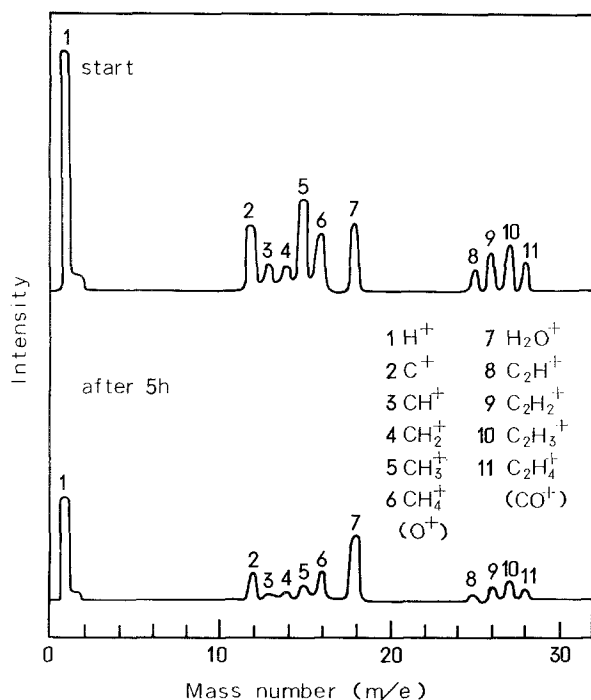


Figure 11 SIMS analysis of Film A.

(2.3) and amorphous carbon (2.0) prepared from isopropane r.f. plasma [1], and slightly lower than for diamond (3.51). Calculation of the diamond content based upon the densities of diamond (3.51) and amorphous carbon (2.0) gives 93 and 86 wt % in Films A and B, respectively.

The values of Vickers hardness of Film A ( $6000 \text{ kg mm}^{-2}$ ) and B ( $5000 \text{ kg mm}^{-2}$ ) measured under a 500 g weight are larger than that of boron carbide ( $3000 \text{ kg mm}^{-2}$ ). Films A and B also show good electrical resistivity ( $10^{12}$  to  $10^{13} \Omega \text{ cm}$ ).

Film B is much less rough than Film A. Smooth surfaces are required for optical coating applications,

making Film B more desirable. The internal stress is relatively high, but smaller than in amorphous carbon ( $\sim 10^8 \text{ N m}^{-2}$ ) prepared from benzene r.f. plasma [2]. The films also have good resistance to corrosive reagents such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{HF}$ .

#### 4. Conclusions

We have obtained very hard, optically transparent and electrically and chemically resistant diamond-like carbon films from  $\text{CH}_4\text{-H}_2\text{-H}_2\text{O}$  mixed gas. These films had a higher growth rate than the  $\text{CH}_4\text{-H}_2$  system, using a microwave plasma. The films have potential applications as coatings for IR and UV optics, machine tools and so on.

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