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PREPARATION AND CHARACTERIZATION

THE PROPERTIES OF DIAMOND-LIKE CARBON FILMS PREPARED BY R.F. DISCHARGES

K. W. WHANG AND H. S. TAE
Department of Electrical Engineering, Seoul National University, Seoul 151–742 (South Korea)
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Diamond-like carbon (DLC) films were produced by r.f. discharge decomposition of methane gas on an r.f.-powered, negatively self-biased electrode. The electrical, optical and mechanical properties of the films are found to be strongly dependent on the deposition conditions. Negative self-bias voltage and gas pressure are shown to be the two most important deposition parameters for accurate control over the properties of DLC films. The electrical resistivity, optical transparency, optical band gap and hardness were examined as functions of the r.f. power and gas pressure.

Also, the crystallographic structure was examined by transmission electron microscopy and diamond microcrystals were observed in DLC films.

An insulating, transparent, very hard film containing diamond microcrystals could be obtained under optimal conditions from the decomposition of CH_4 gas by a 13.56 MHz r.f. discharge.

1. INTRODUCTION

In the past, thin carbon films obtained from the r.f. or microwave discharge of hydrocarbon gases [1–7] or by the carbon ion beam method [8–10] have exhibited unique electrical, optical and mechanical properties which range from polymer like (electrically insulating, mechanically soft and optically transparent) or graphite like (electrically conducting, mechanically soft and optically opaque) to diamond like (electrically insulating, mechanically very hard and optically transparent).

The various physical properties of the resulting films are strongly dependent on the methods and deposition conditions and it has been reported that ions present in the plasma or ion beams play an important role in determining film properties [11–13]. In this work, CH_4 gas was decomposed by a 13.56 MHz r.f. discharge and thin carbon films were deposited on the substrate attached to the powered electrode.

The electrical resistivity, optical transparency and optical band gap of films were examined as functions of the negative self-bias voltage and gas pressure. In particular, the effect of the negative self-bias voltage on these properties was studied

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very carefully. Also, the crystallographic structure was examined by transmission electron microscopy.

2. EXPERIMENTAL METHODS

A schematic diagram of the deposition system is shown in Fig. 1. The chamber is made of stainless steel and has dimensions of 0.3 m (height) × 0.35 m (diameter). CH_4 gas was introduced through the shower-head upper electrode which is grounded, and diamond-like carbon (DLC) films were deposited on various substrates placed on the r.f.-powered lower electrode after generation of a CH_4 plasma between the electrodes. The lower electrode (0.1 m diameter) was water-cooled and covered by a quartz plate (2 mm in thickness). The flow of the gas was controlled by a thermal mass flow controller (Tylan FC-280).

Deposition conditions are shown in Table I. All the depositions were carried out after sputter cleaning the substrate with an argon plasma for 15 min.

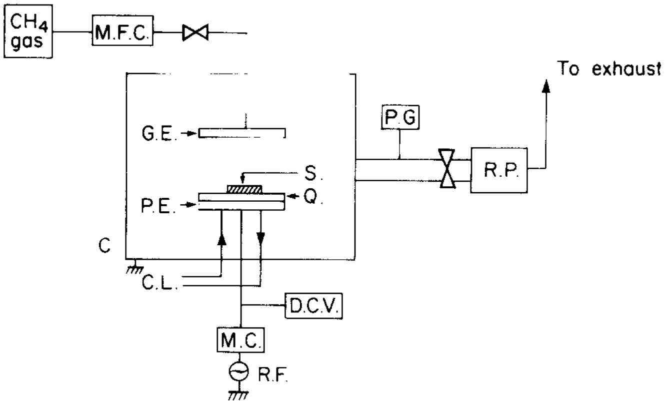

Fig. 1. Schematic diagram of the deposition system.

TABLE I

DEPOSITION CONDITIONS

Substrates	Si wafer, slide glass, stainless steel
R.f. frequency	13.56 MHz
Hydrocarbon gas	CH_4
Gas pressure	0.05–0.5 Torr
R.f. power	30–500 W
Negative self-bias voltage	160–900 V
Distance between electrodes	3 cm
Flow rate	50 standard $cm^3 min^{-1}$

3. RESULTS

3.1. Negative self-bias voltage

The properties of DLC films are dependent on the ion energy impinging on the substrate. The ion energy is determined by the negative self-bias voltage if the ions can pass through the sheath region without collisions with neutrals and ions.

The negative self-bias voltage was measured as a function of the r.f. power and gas pressure. Figure 2 shows the measured negative self-bias as a function of the r.f. power and gas pressure. The negative self-bias increases as the r.f. power increases and tends to be saturated in the region of high r.f. power, but decreases slightly as the gas pressure increases. Therefore, we can note that the negative self-bias voltage depends strongly on the r.f. power and weakly on the gas pressure.

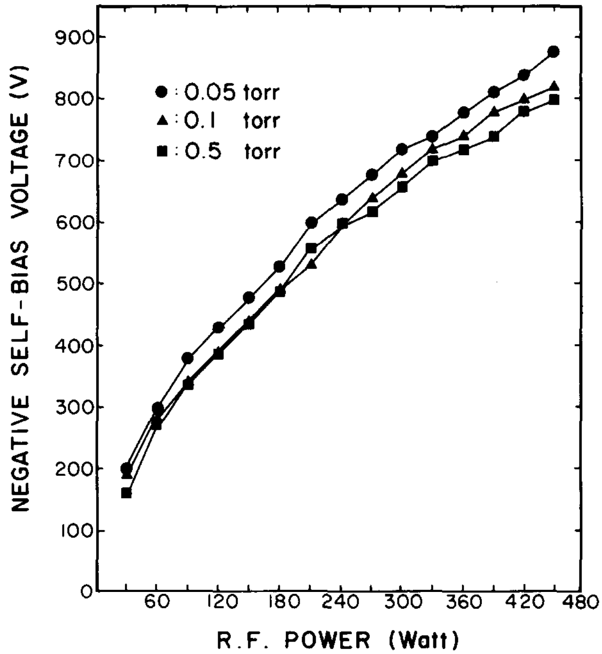

Fig. 2. Self-bias voltage *vs.* r.f. power.

3.2. *Deposition rate*

The thickness and refractive index were measured by ellipsometry at 6328 Å. Figure 3 shows the deposition rate as a function of the r.f. power and gas pressure. The deposition rate ranges from 1.3 Å s^{-1} to 3 Å s^{-1}. At 0.05 Torr the deposition rate increases as the r.f. power increases, but at 0.1 Torr and 0.5 Torr it decreases slightly above 150 W of r.f. power.

3.3. *Refractive index*

Figure 4 shows the refractive index. The refractive index increases as the r.f. power increases to 300 W and increases or decreases thereafter depending on the gas pressure. It has relatively high values, ranging from 2.0 to 2.7

3.4. *Electrical resistivity*

The resistivity was obtained from *I–V* measurements of the sample using the structure shown in Fig. 5. This is made by depositing the DLC on the stainless steel

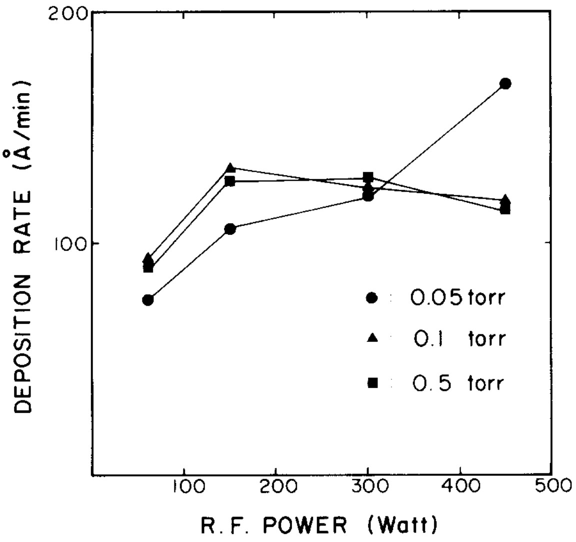

Fig. 3. Deposition rate *vs.* r.f. power.

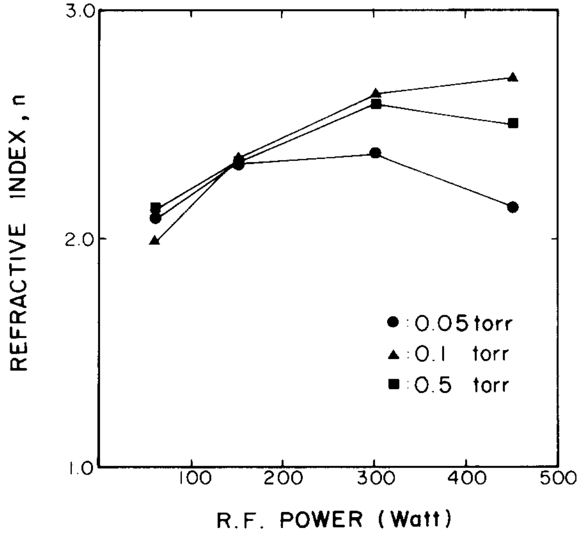

Fig. 4. Refractive index *vs.* r.f. power.

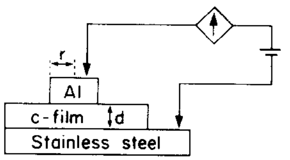

Fig. 5. Resistivity measurement.

substrate and making an ohmic contact on it with aluminium. Figure 6 shows the resistivity.

As shown in Fig. 6(a), when the gas pressure is constant, the resistivity decreases as the r.f. power increases. We can also note from Fig. 6(b) that the resistivity increases as the gas pressure increases when the r.f. power is held constant. Figure 7 shows the resistivity as a function of the negative self-bias voltage under each different gas pressure.

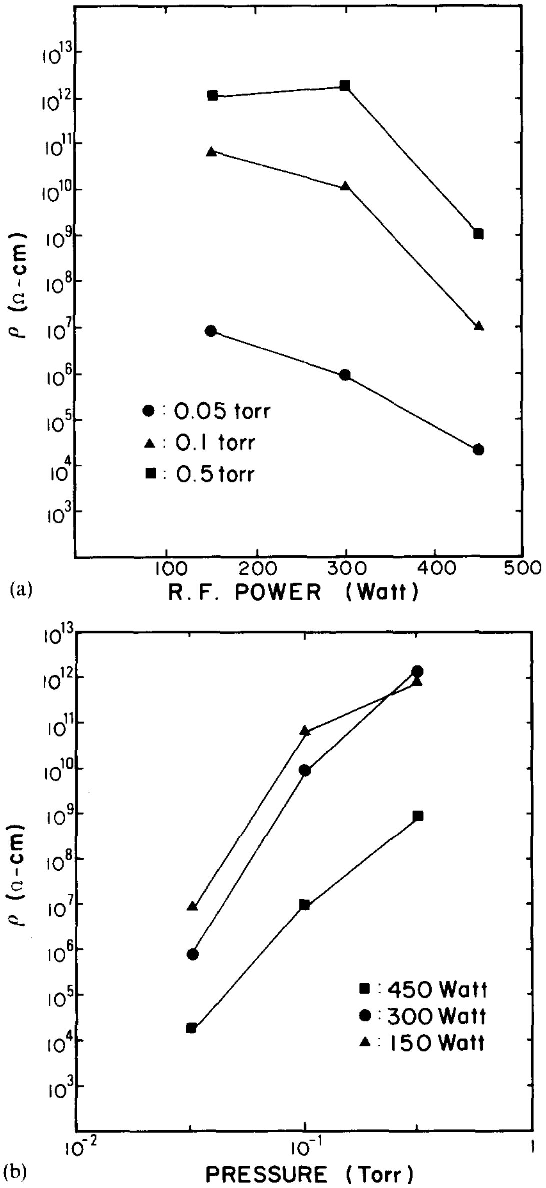

Fig. 6. Resistivity *vs.* (a) r.f. power and (b) gas pressure.

As shown in Fig. 7, the resistivity decreases as the negative self-bias voltage increases when the gas pressure is held constant and also decreases as the gas pressure decreases when the negative self-bias voltage is held constant. From these results, we can note that the resistivity of a DLC film depends strongly on both the negative self-bias voltage and the gas pressure. The breakdown voltage of the DLC film was about 2×10^7 V m^{-1}. Since the energy of the impinging ion is determined by the self-bias voltage and collisions with neutrals, we defined the power density (watts per square centimetre per torr), which is the applied r.f. power per unit electrode area and per unit pressure, as a figure of merit. Figure 8 shows the change in resistivity as a function of the power density.

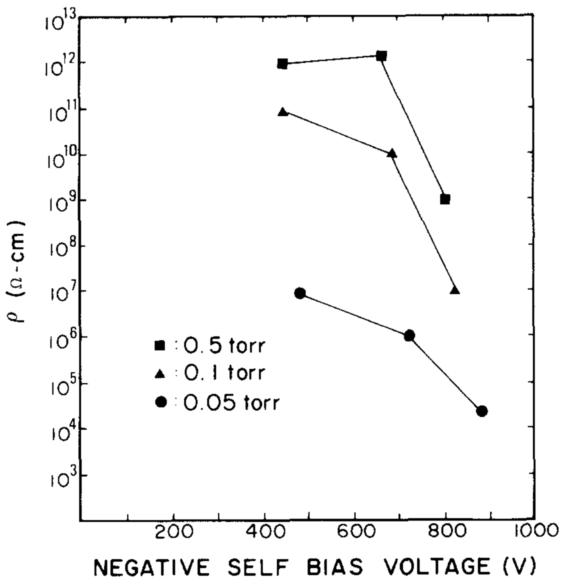

Fig. 7. Resistivity *vs.* self-bias voltage.

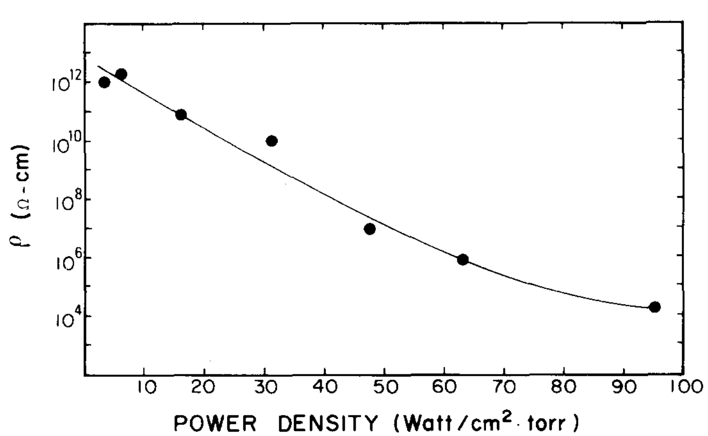

Fig. 8. Resistivity *vs.* power density.

3.5. Optical properties

3.5.1. Optical transmittance

The optical transmittance in the visible and near-UV region is shown in Fig. 9. As shown in Fig. 9, when the gas pressure is constant, the optical transmittance decreases as the negative self-bias voltage increases and, when the negative self-bias voltage is constant, the optical transmittance changes little as the gas pressure varies.

3.5.2. Optical band gap

The optical band gap is determined from the intercept of the extrapolated linear fit to a plot of $(\alpha h\nu)^{1/2}$ *vs.* $h\nu$, where α is the absorption coefficient and $h\nu$ is the photon energy. The changes in the optical band gap E_{og} of DLC films as a function of the deposition conditions, *i.e.* the gas pressure and the negative self-bias voltage, are shown in Fig. 10. These optical properties are found to depend strongly on the negative self-bias voltage but weakly on the gas pressure. Films deposited with a high negative self-bias voltage exhibit lower transmission, higher absorption, especially in the near-UV region, and a lower optical band gap.

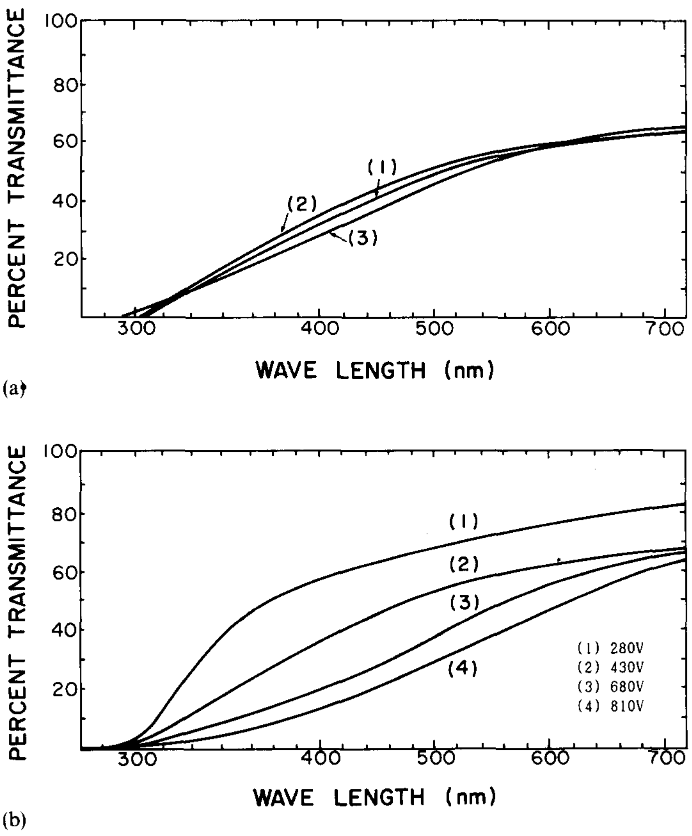

Fig. 9. (a) Optical transmittance for various gas pressures: curve 1, 0.5 Torr; curve 2, 0.1 Torr; curve 3, 0.05 Torr. (b) Optical transmittance for various self-bias voltages: curve 1, 280 V; curve 2, 430 V; curve 3, 680 V; curve 4, 810 V.

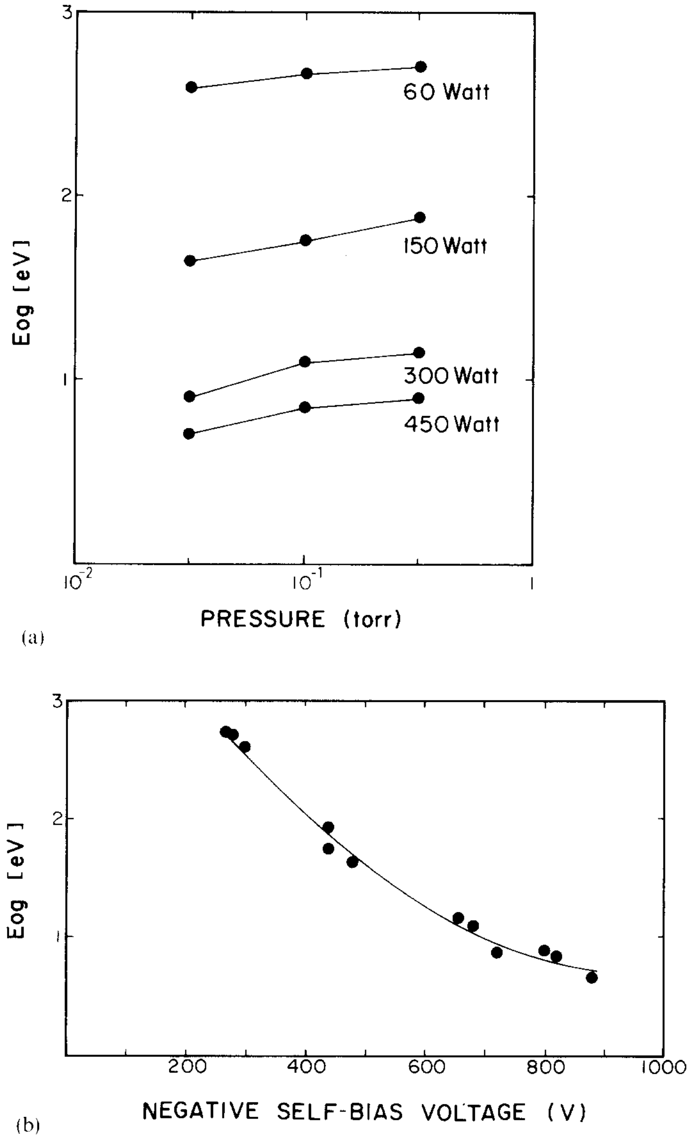

Fig. 10. Optical band gap *vs.* (a) gas pressure and (b) self-bias voltage.

3.6. Mechanical properties: hardness and crystallographic structure

The Vickers hardness of DLC films deposited on silicon wafers was measured and its dependence on the gas pressure and diamond indenter load is shown in Fig. 11. Among the films deposited at various pressures, that deposited at 0.1 Torr has the highest hardness of 3700 kgf mm^{-2} at 2 g load. The hardness changes with the indenter load and this is thought to be due to the peculiar structure of our sample, *i.e.* thin hard films on a soft substrate.

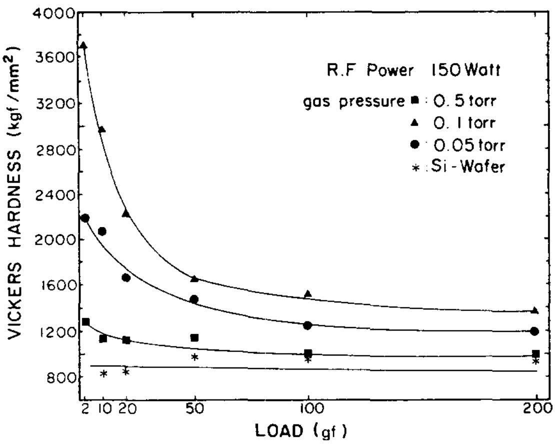

Fig. 11. Vickers hardness *vs.* load.

Transmission electron microscopy was used for the structural investigation of the DLC film obtained at an r.f. power of 150 W and a gas pressure of 0.05 Torr, deposited for 30 min. The transmission electron diffraction dark field and bright field patterns of DLC films were obtained by transmission electron microscopy and are shown in Fig. 12. It was confirmed that the film contained diamond microcrystals of

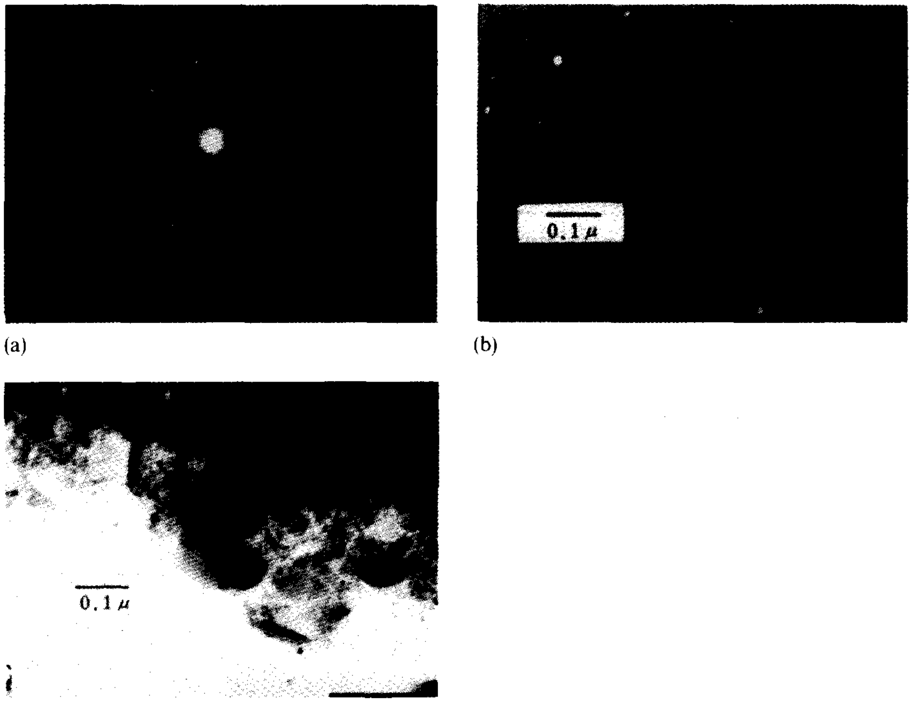

Fig. 12. Transmission electron microscopy results for a DLC film: (a) transmission electron diffraction pattern; (b) dark field; (c) bright field.

sizes 100–200 Å. Interplanar spacings determined from the transmission electron diffraction pattern are shown in Table II and are in good agreement with those of natural diamond. The apperance of a spacing $d = 1.77$ Å was thought to be due to the defects caused by the bombardment with energetic ions during crystal formation.

TABLE II
INTERPLANAR SPACINGS

Measured d spacing (Å)	*Diamond d spacing* (Å)	*hkl*
2.06	2.06	111
1.77		200
1.26	1.261	220
1.07	1.0754	311
0.89	0.8916	400
0.81	0.8182	331

4. CONCLUSION

It has been shown that electrically insulating, optically transparent and mechanically very hard DLC films can be obtained from the glow discharge of methane gas under optimum conditions. Very careful attention was given to examining the role of the parameters which can affect the energy of the substrate-bombarding ions during the film forming process such as the self-bias voltage and gas pressure.

From the structural investigation of the films by transmission electron microscopy, it was confirmed that diamond microcrystals of sizes 100–200 Å were present in the films.

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