

## The effect of H<sub>2</sub>, N<sub>2</sub> and N<sub>2</sub>O doping on DLC thin films deposited by a PECVD method

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Diamond-like carbon (DLC) films were prepared on Si wafers using an rf plasma-enhanced chemical vapor deposition system with the addition of small amount of nitrogen (N<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O) to the gas mixture of CH<sub>4</sub> and H<sub>2</sub>. The deposition rate of films with the addition of N<sub>2</sub>O could be decreased at a rf power of 300 W because of the etching of the surface by the increased oxygen. A Raman band at approximately 2200 cm<sup>-1</sup>, which can be assigned to the C≡N bond stretching mode, was also observed for films with the addition of N<sub>2</sub>. Changes in the Raman intensity with the addition of N<sub>2</sub>O gas were noticeable, indicating a decrease because of the etching of the surface by increased oxygen. The effect of various doping types and level on the thickness, structure, optical properties and surface roughness of DLC films was investigated by ellipsometry, Raman, and AFM characterizations.

**Key words:** Diamond-like carbon, Nitrous oxide (N<sub>2</sub>O), PECVD.

### Introduction

Diamond-like carbon (DLC) thin films exhibit a wide range of mechanical and other interesting physical properties [1-3]. They are for example suitable materials in applications, where it is desirable to increase the transmittance or to reduce unwanted surface reflections [4]. Examples of the former are protective anti-reflective coatings for solar cells. Because DLC films have wide optical band gaps and their refractive indices may be adjusted variably, these films may be utilized as protective and anti-refractive coatings [5, 6]. The criteria for selecting materials and deposition technology for these types of coatings include the useful spectral range of transmission, absorption, scattering, internal stress, environmental stability, film homogeneity, reproducibility, and thermal stability etc.

In order to utilize DLC films for optical applications, it is very important to control the refractive index. Therefore, the primary objective of this study is to investigate the effects of the reactant gas mixture composition and additional gases on the optical band gap. In growing DLC films, hydrogen could be used as an etchant. In contrast to hydrogen, oxygen is expected to reduce the transparency of DLC films. But, it has been shown that the addition of oxygen into the DLC network leads to a substantial improvement of optical

properties and the quality of DLC films [7-9]. Yoshitake et al. also reported that a small amount of oxygen favors diamond nucleation and can enhance diamond deposition while preserving good film quality at higher methane concentrations [10].

In the present study, the optical properties of the coatings were adjusted by the addition of hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>), and nitrous oxide (N<sub>2</sub>O) gas into the deposition feed for DLC deposition in order to obtain coatings with optimum optical properties.

### Experimental Procedures

The DLC films were deposited from appropriate gaseous mixtures of methane (CH<sub>4</sub>), hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>), and nitrous oxide (99.999% N<sub>2</sub>O) using a capacitively-coupled rf PECVD reactor. Substrates were transferred to the reaction chamber via a load lock. The reaction system was a parallel planar discharge system which used a rectangular rf electrode (lower) and a substrate electrode (upper). The substrate was set on a tray with the surface to be coated facing downward, so that the deposition of dust particles and flakes could be minimized. P-type Si wafers with (100) orientation were used as the substrate. Prior to the deposition of films, the wafer was dipped in 10% hydrofluoric acid (HF) for about 40s, rinsed in deionized water and acetone, and finally dried in a nitrogen ambient. Also, the substrates were sputter cleaned in a H<sub>2</sub> glow discharge at a rf power of 60W for 10 minutes. The full range of process parameters for the system is shown in Table 1.

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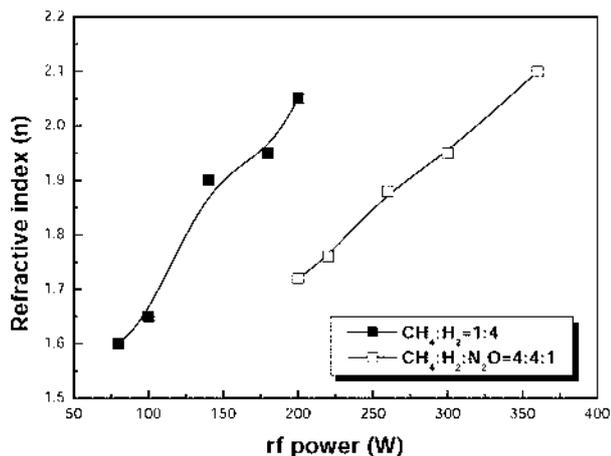
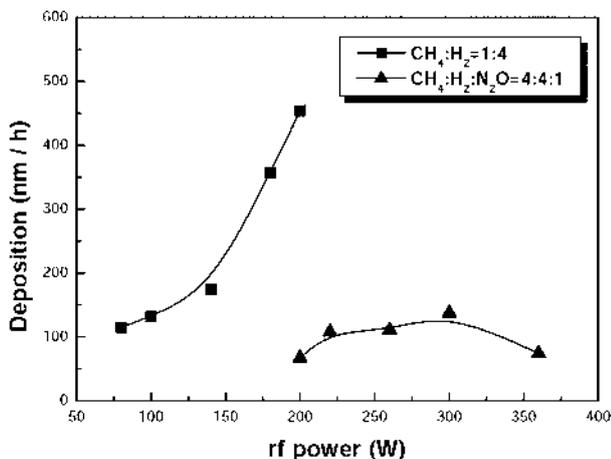
**Table 1.** The process conditions used for the deposition of the DLC films

Parameters	Range
Base pressure	$< 5.3 \times 10^{-3}$ Pa
RF power	80~360 W
Working pressure	53.3 Pa
Substrate Temperature	Room temp.
CH <sub>4</sub> : H <sub>2</sub> : N <sub>2</sub> O ratio	4 : 4 : 1

The refractive index and the thickness of the DLC films were measured by ellipsometry at  $\lambda = 1552$  nm. The effect of rf power and amount of N<sub>2</sub>O gas on the structure and surface roughness of DLC films were investigated by Raman and AFM characterizations.

## Results and Discussion

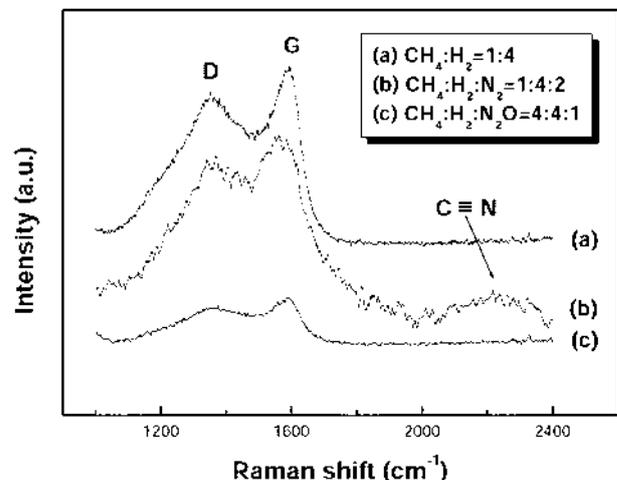
The variation in the refractive index is shown in Fig. 1. As can be seen from Fig. 1 both H<sub>2</sub>, and N<sub>2</sub>O in the film-forming gas mixture may satisfy this condition under some parameters of the deposition process. We

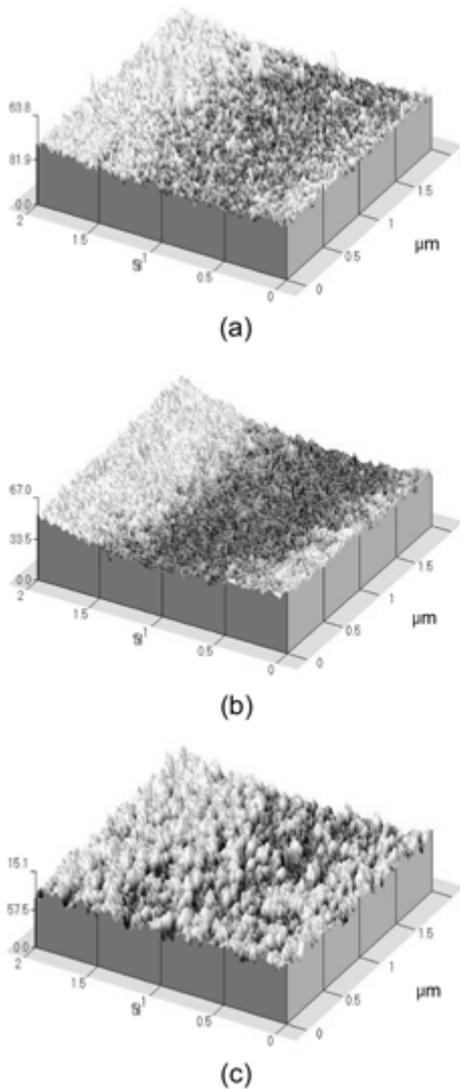
**Fig. 1.** The variation of refractive index for H<sub>2</sub> gas addition films and N<sub>2</sub>O gas addition films as a function of rf power.**Fig. 2.** The deposition rate for H<sub>2</sub> gas addition films and N<sub>2</sub>O gas addition films with rf power.

can see that the density of the DLC film increases with the rf power. This implies that the energy of the ions increased with increasing rf power, that is, they are severely bombarded by the ions.

Figure 2 shows the deposition rate of films with H<sub>2</sub> and N<sub>2</sub>O gas additions on Si substrates with the rf power ranging from 80 to 360 W. The deposition rate for H<sub>2</sub> gas films increases to 454 nm/h on increasing the rf power from 80 to 200 W, because of the reactive gas, the ionization rate and the plasma density increased and we can imagine that the deposition rate has been increased by them. Increasing the rf power for N<sub>2</sub>O gas films leads to the production of more radicals and to a deposition rate as high as 138 nm/h at 300W, after which it decreased. The deposition rate at 200W is similar to that at 360W. The deposition rate has been compared between those without N<sub>2</sub>O and those with N<sub>2</sub>O. The deposition rate with N<sub>2</sub>O was smaller than that without N<sub>2</sub>O. We can explain this in terms that the deposition rate of N<sub>2</sub>O film could be decreased at a rf power of 360W because of the etching of the surface by the increased oxygen. Regarding the optimum oxygen content, it was proposed that a high oxygen content should be used for etching non-diamond components in a growing film, and a low oxygen content for deposition to achieve a higher growth rate without sacrificing film quality [11].

Raman spectroscopy is commonly used to analyze the macroscopic bonding structure of carbon-related materials. Figure 3 shows that the main features of the spectra obtained are the D and G bands characteristic of DLC films. These two bands are common to all disordered polycrystalline and amorphous graphitic carbons; they are found in the region 1530-1600 cm<sup>-1</sup> (G band) and at approximately 1360 cm<sup>-1</sup> (D band), depending on the sample preparation procedures. The peak at 1360 cm<sup>-1</sup> may be due to the sp<sup>3</sup>-hybridized carbon content in the film, whereas the other peak at 1530 cm<sup>-1</sup> may be due to disordered sp<sup>2</sup> hybridization

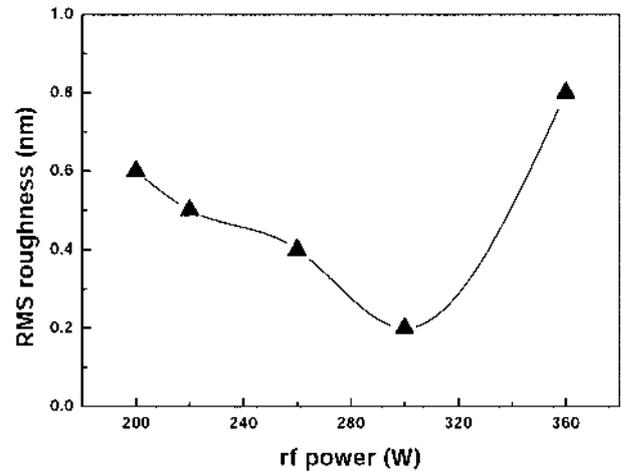
**Fig. 3.** The Raman spectra of H<sub>2</sub>, N<sub>2</sub>, and N<sub>2</sub>O gas addition films.



**Fig. 4.** AFM image ( $2 \times 2 \mu\text{m}$ ) on rf power of (a) 200 W, (b) 300 W, and (c) 360 W.

[12, 13]. A small Raman band at approximately  $2200 \text{ cm}^{-1}$ , which can be assigned to the  $C\equiv N$  bond stretching mode, was also observed for films with  $N_2$  additions in the deposition gas (Fig. 3(b)). This implies that the number of carbon atoms in the carbon-nitrogen triple bonds increased with the addition of  $N_2$ . The influence of the  $N_2O$  addition to the process gases in the preparation can be inferred by inspection of sample (a) and (c) of Fig. 3. Changes in the Raman intensity with addition of  $N_2O$  (Fig. 3(c)) is noticeable, indicating a decrease because of the etching of the surface by the increased oxygen.

Figure 4 shows AFM images ( $2 \times 2 \mu\text{m}^2$ ) of the surface morphology of films in the processing of  $N_2O$  at various rf powers, ranging from 200 to 360 W. Figure 5 shows the variation of the root-mean-square (RMS) roughness of the  $N_2O$  gas deposited films with increasing rf power to confirm the role of  $N_2O$  gas. At a rf power of 200 W, the RMS roughness is larger since the



**Fig. 5.** The RMS roughness of DLC films at various rf power.

kinetic energy of the ions at this smaller rf power is insufficient to remove certain asperities and hence to smooth the film surface. As the rf power increases, the RMS roughness decreased. With even more rf power a higher RMS roughness appear. However, as the rf power is increased with a limited flow ratio, activated radicals that have higher surface mobility were created. Activated radicals contribute to reduce RMS roughness because of mobility from the film surface to the lower surface region. It can be seen from the AFM images in Fig. 4 that surface roughness for the films deposited at a larger rf power of 300 W was smoother. At an even larger rf power than 300 W, a RMS roughness of 0.2 nm was obtained. The RMS roughness for films deposited at a larger rf power of 360 W was too high (0.8 nm). These phenomena were due to the etching of the surface by increased oxygen.

## Conclusions

We have fabricated high quality diamond-like carbon (DLC) films using a PECVD method with  $CH_4$ ,  $H_2$ ,  $N_2$ , and  $N_2O$  gas mixtures. The deposition rate for the  $H_2$  gas film increases to 454 nm/h on increasing the rf power from 80 to 200 W, because of reactive gases, ionization rate and increased plasma density. The deposition rate with  $N_2O$  was smaller than that without  $N_2O$ . The deposition rate of  $N_2O$  films could be decreased at a rf power of 360 W because of the etching of the surface by the increased oxygen. A small Raman band at approximately  $2200 \text{ cm}^{-1}$ , which can be assigned to the  $C\equiv N$  bond stretching mode, was also observed for the  $N_2$  addition film (Fig. 3(b)). This implies that the number of carbon atoms in the carbon-nitrogen triple bonds increased with the addition of  $N_2$ . Changes in the Raman intensity with the addition of  $N_2O$  (Fig. 3(c)) are noticeable, indicating a decrease because of the etching of the surface by the increased oxygen. At a rf power of 200 W, the RMS roughness is

larger since the kinetic energy of the ions at this smaller rf power is insufficient to remove certain asperities and hence to smooth the film surface. As the rf power was increased, the RMS roughness decreased.

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