

## The effect of nitrogen doping in a-C:H films using plasma enhanced chemical vapor deposition method

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Nitrogen doped hydrogenated amorphous carbon (a-C:H) films were prepared by rf PECVD (plasma enhanced chemical vapor deposition) method using CH<sub>4</sub>, H<sub>2</sub> and N<sub>2</sub> gases. The optical band gap (E<sub>opt</sub>) decreased from 2.3 eV to 1.9 eV with increasing nitrogen content. Infrared absorption analysis showed that NH<sub>2</sub> spectra appeared and that CH, CH<sub>2</sub> and CH<sub>3</sub> spectra decreased with increasing nitrogen content. The nitrogen content in a-C:H films was examined by XPS (X-ray photoelectron spectroscopy). It appears that the role of nitrogen is to break the C-H, C-H<sub>2</sub>, C-H<sub>3</sub> bonds and to form a C-N-H<sub>2</sub> bond but it does not create three-dimensional cross-linking of the carbon skeleton.

### 1. Introduction

Thin films of hydrogenated amorphous carbon (a-C:H) have potential as the material of modern electronic devices such as light emitting diodes and magnetic recording device etc.. However, it is unsatisfactory for these practical applications because the large number of lattice defects (e.g., dangling bond) in a-C:H degrades the required device performance. The presence of these defects underlines the fact that the fundamental understanding of optical, electronic and structural properties of a-C:H is not complete.

In order to investigate the optical properties related to the lattice defects, we have used the PECVD method to prepare a-C:H films. This method is a very popular technique used for the growth of a-C:H films and is suitable for the preparation of large and homogeneous areas. We have measured the optical absorption coefficient and infrared absorption of N (nitrogen) doped a-C:H films.

### 2. Experimental details

Nitrogen doped a-C:H films were prepared by the rf PECVD method. The scheme of the experimental

equipment is illustrated in Fig. 1. The PECVD deposition reactor is of stainless steel. All substrates were cleaned ultrasonically in sequence in the PECVD system. Prior to deposition the system was evacuated by a turbo-pump having sufficient pumping speed for water and other residual gases to attain a background pressure better than  $5 \times 10^{-7}$  Torr. The power supply unit was a 13.56 MHz rf generator with a maximum power of 1000 W. The diameter of the parallel electrodes was 10 cm and the electrode separation was 2 cm. The grounded substrate holder could be heated to 500 °C or cooled by air to room temperature. Total gas pressure was fixed at 0.1 Torr with a gas flow rate of 50 ccm. The rf power was maintained at 20 W and the substrate bias voltage was between -0.24 kV ~ -0.26 kV. During the deposition process the substrate temperature was normally maintained at about 40 °C. Pure methane, nitrogen and hydrogen gases were used as source gases. The fraction (x) of CH<sub>4</sub>+N<sub>2</sub> gases ( $(\text{CH}_4+\text{N}_2)/(\text{CH}_4+\text{N}_2+\text{H}_2)$ ) was kept at 20 % and the ratio of N<sub>2</sub> to CH<sub>4</sub> was varied from 0 % to 50 %. The thickness of the a-C:H films was about 0.1 μm.

Quartz substrate samples, whose thickness was measured on a Kosaka Laboratory Model SE-3 instrument, were used for the optical absorption

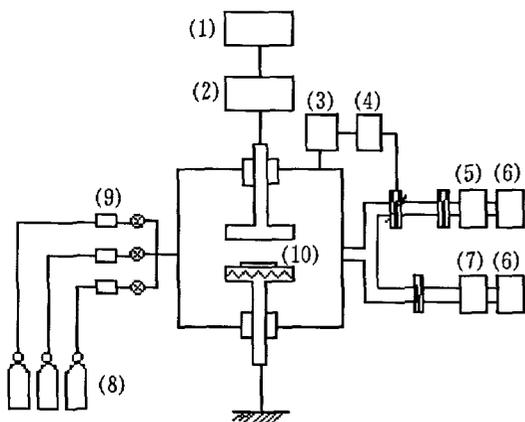


Fig. 1. Schematic representation of the plasma enhanced chemical vapor deposition system. (1) RF generator, (2) matching box, (3) vacuum gauge, (4) automatic pressure controller, (5) mechanical booster pump, (6) rotary pump, (7) turbo pump, (8) feed cylinder, (9) mass flow controller, (10) substrate

measurements. The optical absorption spectra of a-C:H with varying amounts of nitrogen were measured on a Hitachi Model U-3400 spectrophotometer in the range  $\lambda=0.185\sim 2.5\mu\text{m}$  covering the UV, visible and near IR region. The infrared absorption spectra of N doped a-C:H were measured on a Jasco Model FT-IR 8900- $\mu$

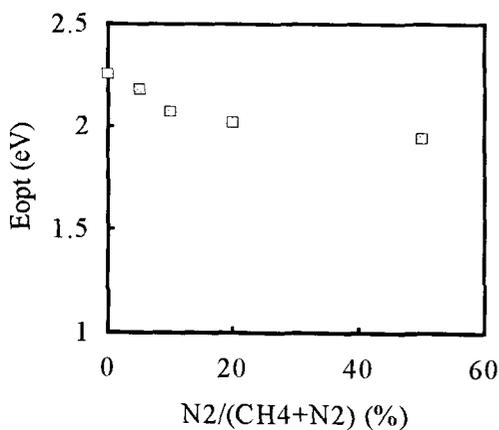


Fig. 2 The optical gap of the a-C:H films prepared by plasma enhanced chemical vapor deposition as a function of the fraction of nitrogen gas.

spectrometer using an intrinsic Si substrate.

### 3. Results and discussion

#### 3.1 Optical properties of nitrogen doped a-C:H

The films were transparent in the visible region and yellow in color. The optical properties of our films were studied by optical absorption. The optical band gap ( $E_{opt}$ ) of nitrogen doped a-C:H was determined from Tauc plots. The high energy ( $h\nu > 2.5$  eV) region of the optical absorption coefficient  $\alpha$  can be described by the equation,

$$\alpha h\nu = B(h\nu - E_{opt})^2$$

where B is constant. Plots of  $E_{opt}$  as a function of nitrogen content are shown in Fig. 2. On increasing the  $N_2/(CH_4+N_2)$  ratio,  $E_{opt}$  decreases from about 2.3 eV to about 1.9 eV.

Deviation from linearity at low energy in the Tauc plot arises from transitions in exponential band tails below the absorption edge. The low energy ( $h\nu < 2.5$  eV) region of  $\alpha$  is given by

$$\alpha = \alpha_0 \exp(h\nu/E_u)$$

where  $E_u$  is the Urbach energy. Fig. 3 shows the nitrogen content dependence of the Urbach energy. As the  $N_2/(CH_4+N_2)$  ratio increases the value of  $E_u$  for a-C:H films remains constant up to 10 %  $N_2/(CH_4+N_2)$  and then increases continuously. The

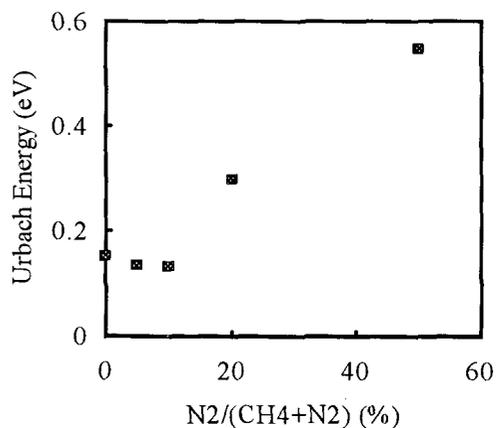


Fig. 3 Urbach Energy of the a-C:H films prepared by PECVD as a function of the fraction of nitrogen gas.

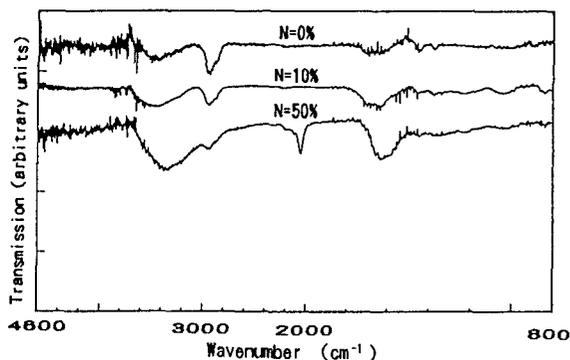


Fig. 4 The IR absorption spectrum from nitrogen doped a-C:H films for nitrogen content  $N_2/(CH_4+N_2)$  0%, 10% and 50%.

Urbach energy is related to the degree of structural disorder in the amorphous network. As the width of the band tails increases with increasing Urbach energy, the addition of nitrogen into a-C:H modifies the density of states near the band edge and the increase in the nitrogen content increases the structural disorder of the films.

### 3.2 Film composition

Fig. 4 shows infrared absorption spectra of three a-C:H films in the range 800~4500  $cm^{-1}$ . Comparing these spectra with those of known a-C:H and nitride molecules, we can identify the main peaks as follows: 2960  $cm^{-1}$ , 2925  $cm^{-1}$ , and 2870  $cm^{-1}$  correspond to  $sp^3CH_3$  asymmetric and  $sp^3CH+sp^3CH_2$  asymmetric and  $sp^3CH_3$  symmetric stretching modes respectively[1-3]. The 1450  $cm^{-1}$  and 1370  $cm^{-1}$  peaks correspond to C- $CH_3$  asymmetric and C- $CH_3$  symmetric deformation modes respectively. Furthermore the 3335  $cm^{-1}$  and 1615  $cm^{-1}$  peaks are for  $NH_2$  stretching and deformation modes. Both broad  $NH_2$  stretching at  $\sim 3335$   $cm^{-1}$  and  $NH_2$  deformation modes at  $\sim 1615$   $cm^{-1}$  spectra have increased and CH spectra at 2870~2960  $cm^{-1}$ , 1450  $cm^{-1}$  and 1370  $cm^{-1}$  have decreased for a-C:H films with increasing nitrogen content. From these results, it is suggested that nitrogen atoms break the C-H, C-H<sub>2</sub>, C-H<sub>3</sub> bonds and form a C-N-H<sub>2</sub> bond.

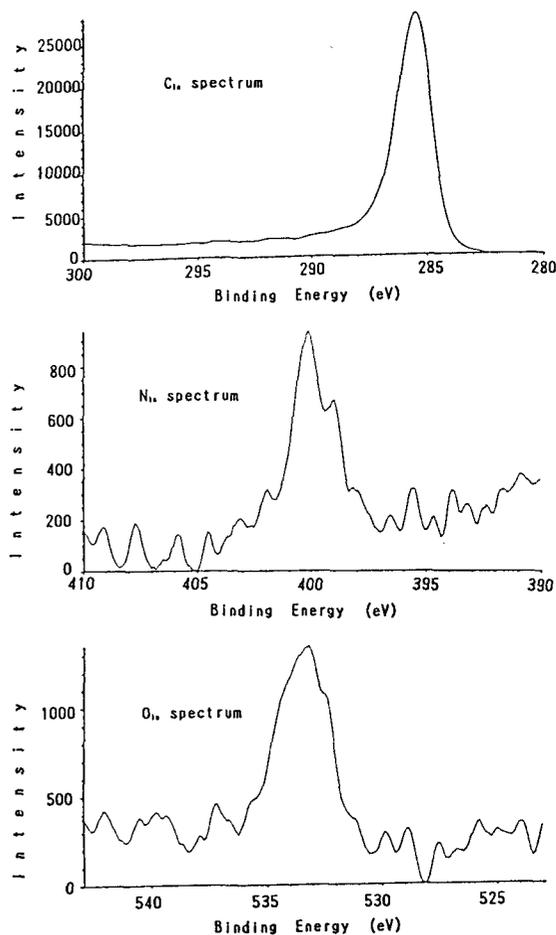


Fig. 5 XPS spectra of a-C:H film with 10 % nitrogen content  $N_2/(N_2+CH_4)$

### 3.3 Nitrogen content

Fig. 4 shows a XPS spectrum from a 10 %  $N_2/(CH_4+N_2)$  film deposited on fused quartz glass. From this figure we can identify the main spectrum as follows;  $\sim 288$  eV,  $\sim 400$  eV and  $\sim 530$  eV are related to carbon, nitrogen and oxygen spectra respectively. The content of nitrogen is 1.7 atomic % and that of oxygen as contamination is 2.0 atomic % from the results of quantitative analysis. Since nitrogen does not form a solid at

room temperature, it must be bonded with carbon in some way. This result supports the IR measurements.

#### 4. Conclusion

The results of this work can be summarized as follows;

- (1) The optical gap of nitrogen doped a-C:H films decreased from 2.3 eV to 1.9 eV when nitrogen concentration varied from 0 % to 50 %. This indicates that the disorder of the amorphous network is enhanced by nitrogen atoms in a-C:H.
- (2) The Urbach energy of nitrogen doped a-C:H increases from 0.1 eV to 0.6 eV with nitrogen content  $N_2/(N_2+CH_4)$  increases from 0 % to 50 %, showing the increase in width of band gap.

(3) From the infrared absorption measurements it is shown that the introduced nitrogen atoms in a-C:H form  $NH_2$  bonds and terminate the C-H structures, but does not contribute for creation of three-dimensional cross-linking of the carbon skeleton.

#### References

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