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Fabrication of a-CN_x:H films with high nitrogen content by RF-plasma CVD of the CH_3CN/N_2 gas mixture

CH_3CN/N_2混合気体の高周波プラズマCVDを用いた高窒素含有 a-CN_x:H薄膜の形成

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Hydrogenated amorphous carbon nitride (a-CN_x:H) films were formed by using a parallel-plate radio-frequency (RF) plasma chemical vapor deposition (CVD) of the gas mixture of CH_3CN and N_2 where Ar was used as a buffer gas. The total pressure of Ar+N_2 were 0.3 Torr, whereas the partial pressure of CH_3CN was suppressed to <10 mTorr. The compositional analysis was made by X-ray photoelectron spectroscopy (XPS), yielding [N]/([N]+[C])=0.30-0.45. The chemical structure of films were analyzed by using infrared absorption, Raman, and a high-resolution XPS.

1. Introduction

In the fabrication of thin films of carbon nitrides, it has been the central problem to incorporate N atoms into the C-C network of films as much as possible [1]. The reason for this chemical design is as follows. Since the length of the C-N bond (1.48 Å) is shorter than that of the sp^3-hybridazed C-C bond (1.54 Å) [2], high mechanical hardness is expected if the network of C-N bond is developed. In the well-known method of plasma-enhanced chemical vapor deposition (PECVD) using radio-frequency (RF) discharge of the gas mixture of N_2 and organic materials such as CH_4, the nitrogen contents or the [N]/([N]+[C]) ratios of films have been suppressed to be <0.1 [3]. Therefore, the methodology to incorporate N atoms has been required. In this study, we have developed a method for this purpose using conventional parallel-plate RF-plasma CVD using the gas mixture of Ar+N_2+ CH_3CN.

2. Experiments

Fig. 1 shows the schematic diagram of the apparatus of RF-plasma CVD. It consists of a stainless-steel chamber of the diameter of 254 mm. A pair of electrodes was placed inside of the chamber. Ar and N_2 were introduced with the total pressure of 0.3 Torr, where their partial pressures, P_{Ar} and P_{N2}, respectively, were varied as listed in Table 1. A 13.56 MHz RF power of 50 W (Tokyo High Power, A-500) was applied to the upper electrode through a matching box (Tokyo High Power, HC-2000S). The lower electrode was grounded. Then, CH_3CN was introduced from a Pyrex-glass nozzle whose orifice diameter was ≈1 mm. The partial pressure of CH_3CN was <10 mTorr, although precise measurement was impossible because it was much lower than that of Ar or N_2. Films were deposited onto Si substrates placed both onto upper and lower electrodes. The deposition time was 3 h.

Films were analyzed by use of Fourie-transformed infrared (FTIR) absorption spectroscopy (Nicolet 6700), Raman scattering (Renishaw 2000), and X-ray photoelectron spectroscopy (XPS) (JEOL JPS-9010).

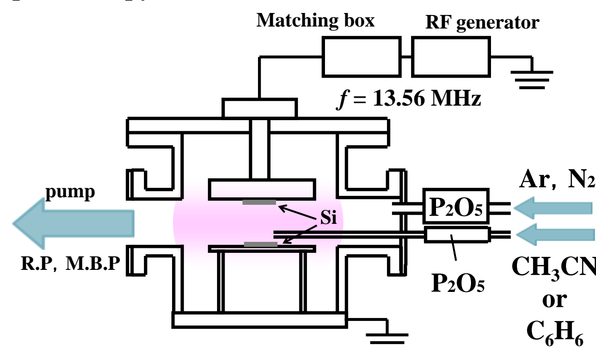

Fig. 1 RF-plasma CVD apparatus.

3. Results and discussion

Table 1 lists the results of the compositional analysis. In addition to the C and N atoms, significant amount of O atoms were detected. The [N]/([N]+[C]) ratios are plotted against P_{N2} as shown in Fig. 2. These ratios exhibit 0.30-0.45, being much higher than the previous reports. Figs. 3(a) and 3(b) show the high-resolution XPS spectra of the C(1s) and N(1s) states, respectively, for the films formed on the lower electrode under the condition of P_{N2}=0.1 Torr. The C(1s) spectra were

Table 1 Experimental conditions and compositional analysis

P_{Ar} [Torr]	P_{N2} [Torr]	C	N	O
0.3	0.0	61.0±1.0	26.0±1.0	13.0±0.5
0.2	0.1	57.5±0.5	37.0±0.0	5.5±0.5
0.1	0.2	51.0±2.0	43.5±2.5	5.5±0.5
0.0	0.3	59.5±0.5	33.5±2.5	7.0±3.5

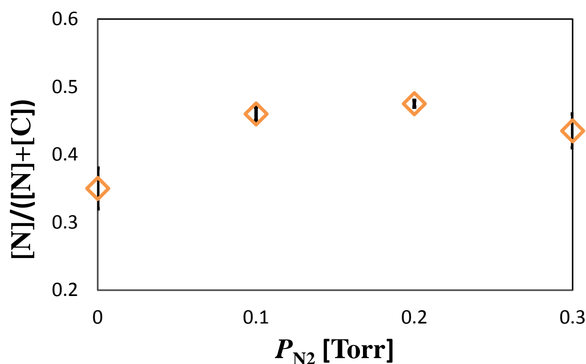

Fig. 2 [N]/([N]+[C]) ratios of films.

fitted satisfactorily by Gaussian profile of C=N bond with smaller contributions of C=C and C-C bonds [4]. The N(1s) peak was fully explained by a single Gaussian profile of N=C bond [5]. These results indicate that the network of films were dominated by C=N bonds; the incorporation of N_2 gas was negligible. Fig. 4 shows the FTIR spectra of the films deposited onto the upper electrode. The G- and D-bands were observed in the region of ≈1550 and ≈1400 cm^{-1}, respectively [6], where the G-band may be overlapped by C=N stretching vibration. With the consideration of the result of XPS, the assignment of C=N seems to be correct for the ≈1550 cm^{-1} band. NH_y (y=1,2) stretching vibration was observed around 3300 cm^{-1}. The C≡N stretching vibration at 2300 cm^{-1} was rather weak. In addition, weak C-N stretching vibration was observed around 1300 cm^{-1}. All these vibration modes were almost independent of P_{N2}, whereas the CH_z (z=1-3) stretching vibration modes observed around 2800 cm^{-1} were dependent on.

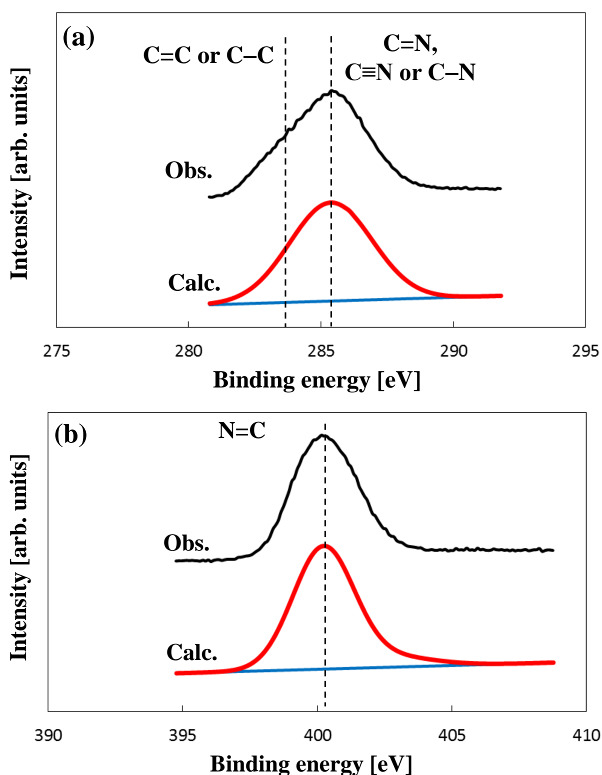

Fig. 3 High resolution XPS spectra (upper trace) and the result of the simulation analysis (lower trace). (a) C(1s). (b) N(1s).

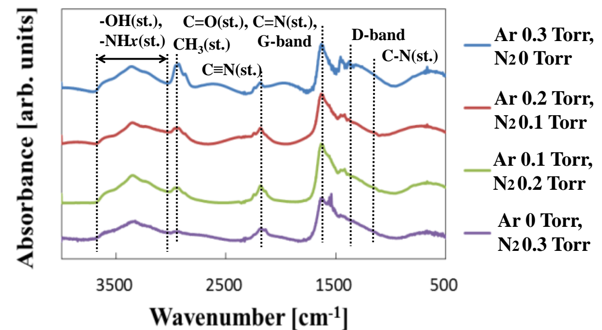

Fig. 4 FTIR spectra.

4. Conclusion

This study reports on the novel methodology to fabricate a-CN_x:H films with high nitrogen content. The essential point may be the suppression of the partial pressure of organic vapor compared to the total pressure. The chemical structure of films may dominate the C=N network. The CH_z and C≡N groups usually observed in the films with low nitrogen content decrease their densities in the present films.

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