Study of Amorphous Carbon Nitride Films Aiming at White Light Emitting Devices

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The possibility for white light emitting devices using carbon nitride (CNx) thin films has been studied. Microwave ECR-plasma CVD and RF-sputtering apparatuses have been used for the formation of CNx thin films. In both cases, CH_4 was used as the source or sub-source of carbon in order to investigate the effect of hydrogenated carbon nitride for luminescence. The cathodeluminescence (CL) measurement of the film grown by ECR-plasma CVD method showed three peaks of R/G/B. The photoluminescence (PL) measurement of the film grown by RF-sputtering also showed the red peak, which could not be observed in the film without hydrogen. Together with the X-ray Photoelectron Spectroscopy (XPS) analysis data, we concluded that the red peak originates from C-H bonds and blue peak from C-N bonds.

KEYWORDS: white light emitting device, hydrogenated carbon nitride, spectrum, C-H bond, C-N bond

1. INTRODUCTION

1.1. Background

Recently blue LEDs (Light Emitting Diode) using GaN semiconductor are commercialized and we can compose the white light by using the red, green and blue LEDs. Today the white LEDs composed by applying the yellow phosphors to the blue LEDs are put to practical use. The white LED has great advantages, compared with the conventional light sources such as fluorescent lamps. For example, the power consumption is expected to be almost the half of a fluorescent lamp, toxic substance such as mercury is not used in the device, and it has long lifetime of about 100,000 hours, that is, 11years. However white LED has also disadvantages to be solved. For example, it is high cost because the blue LED that is used for composing white light uses sapphire substrate, and it has not a good color rendering property due to being composed by applying only yellow phosphors to the blue LED.

Meanwhile, optical characteristics such as photoluminescence:PL[1],cathodeluminescence:CL[2] and electroluminescence:EL[3] as for amorphous carbon nitride (a-CNx) have been reported.

Especially, R.Reyes et al. showed the white-blue EL emission at room temperature using a-CNx for an applied voltage of 6V.[3] The EL structure is shown in Fig. 1, in which an indium tin oxide (ITO) layer is used as transparent anode while an Al film is used as the cathode and the emitting layer is an a-CNx thin film.

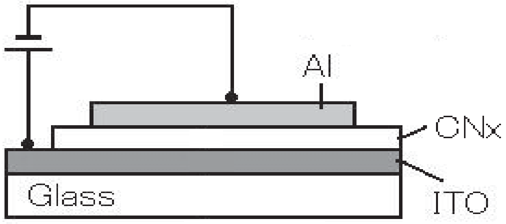

Figure 1 Emitting light device configuration[3]

They showed that the EL spectra peaked at 475nm (2.6eV), but red emission was not observed. On the other hand, H.K.Jang et al. observed the 2.16eV yellow peak for a-CNx film. In this case methane (CH_4) gas was used as the source of carbon.

Nitta et al.[4] suggested the model of density of state about a-CNx shown in Fig. 2. They reported that the transition whose energy is 1.4eV～1.9eV is interband transition between π^* conduction band and lone-pair valence band of nitride. This is equivalent to the optical energy gap (Tauc Energy). According to this model, the transition whose energy is more than 2eV occurs between π^*conduction band and π valence band , or σ^* conduction band and lone-pair valence band.

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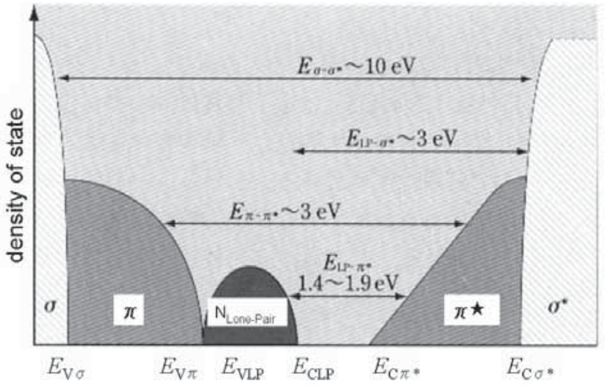

Figure 2 Model of density of state about a-CNx4)

1.2. Background

Under these backgrounds, the purpose of this study is to investigate the possibility for white light emitting device using a-CNx. In this paper, we report on a-CNx thin films prepared by using ECR-plasma CVD apparatus and RF-sputtering apparatus. In both cases, CH$_4$ was used as the source or sub-source of carbon in order to investigate the effect of hydrogenated carbon nitride for luminescence in more detail.

2. EXPERIMENT

2.1. Fabrication by Microwave ECR-plasma CVD

Figure 3 shows the ECR-plasma CVD apparatus that was used for this study. N$_2$ and CH$_4$ were used as reactive gases and flowed into the evacuated plasma chamber. We applied Microwave (2.45GHz) power to mix gas in the condition of ECR and made plasma in the chamber and deposited a-CNx on the aluminum substrate. Deposition of a-CNx was performed in the condition that microwave power was 180W and synthesis time was 24hour, and gas flows of N$_2$ and Ar are 100sccm and 0.8sccm, respectively.

Cathode Luminescence (CL) measurement was performed in the case of CN$_{1.04}$ film. In measuring CL intensity, we used CL-SEM in the conditions that accelerating voltage is 15kV, current is 1nA, temperature is RT, and measured area is 185×220μm^2. The result is shown in Fig. 4. As seen in Fig. 4, CL spectrum of a-CNx has three peaks. The peak of 2.14eV is red (580nm), and 2.56eV is green (480nm), and 3.10eV is blue (400nm). This spectrum includes three colors of R/G/B covering the white color region, as shown in Fig. 5.

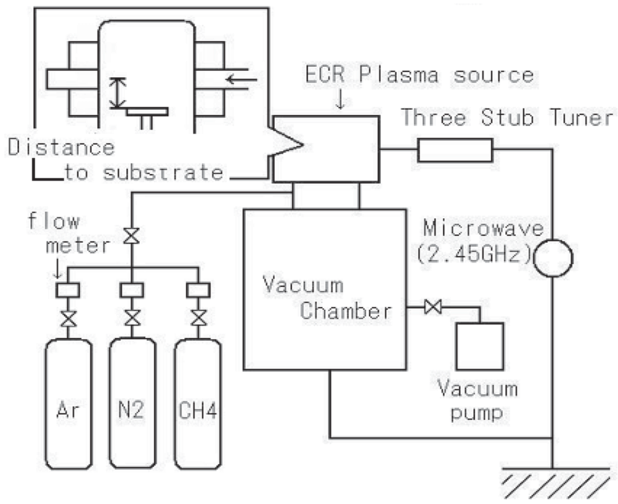

Figure 3 ECR-plasma CVD apparatus

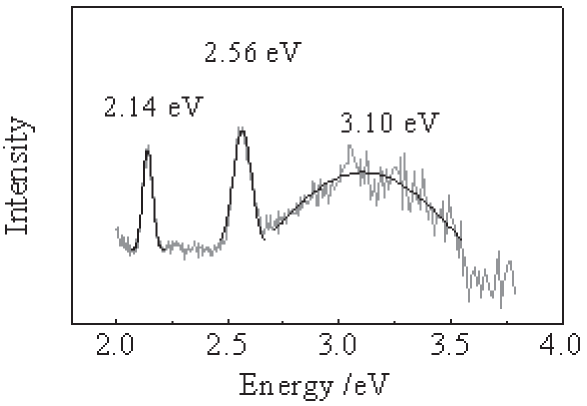

Figure 4 Cathode Luminescence measurement result

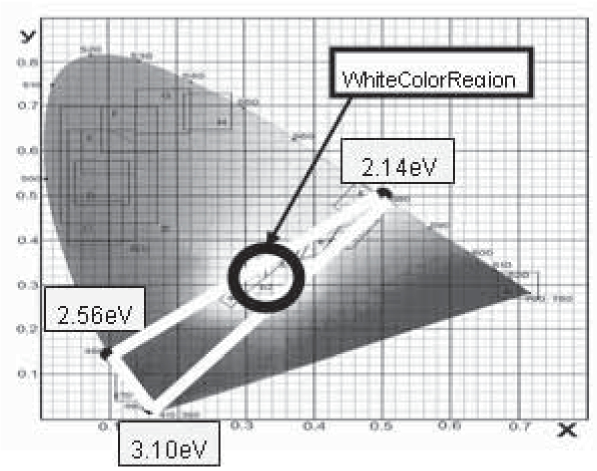

Figure 5 Plot of 3 peaks on Color Diagram

As for the Electoroluminescence (EL) emission reported by R.Reyes[3)], C-H bond is not included because it is composed in no hydrogen condition. As a result, only the blue emission was observed due to C-N bonds. On the other hand, the CNx film that was composed using microwave ECR-plasma CVD in this time has the emission of red light possibly due to C-H bonds[1)] because it is composed in a condition including hydrogen. Therefore, we can expect white light emission with good color rendering by controlling the red peak originated from C-H bonds, and green and blue peaks originated from C-N bonds.

2.2. Fabrication by RF-sputtering

The feature of the film fabricated in this time by using RF-sputtering method is the use of CH_4 gas in addition to the N_2 and Ar gases. The reason is that the use of CH_4 may increase the C-H bonds, which is considered to be the origin of red light, as described in 2.1.

N_2 and Ar and CH_4 were used as reactive gases and flowed into the plasma chamber. After the chamber was evacuated until 2.0×10^3 Pa, N_2 and Ar gas were flowed into the chamber and the pressure was kept to 0.8Pa. Ar gas was flowed to make the discharge stable. The ITO deposited glass substrate was etched under the condition that RF-power was 100W×10min and the carbon target was pre-sputtered under the condition that RF-power was 500W×60min. The substrate bias was –100V and the substrate temperature were 100V.

Figure 6 shows the experimental result of nitrogen concentration in the grown film as a function of flow gas ratio of N_2/Ar. It is seen that the higher the ratio of N_2/Ar the higher the nitrogen concentration in the film. But nitrogen concentration seems to saturate at about 30%. It might be difficult to increase the nitrogen concentration more than 30% by using N_2 and Ar gases simultaneously in RF-sputtering method.

The characteristics of a-CNx(H) films which were obtained under the condition that N_2 and Ar gas flows were 8.0sccm and 2.0sccm respectively (N_2/Ar =4.0) were investigated by using the X-ray Photoelectron Spectroscopy (XPS) and optical absorption. In this case, CH_4 gas flow was changed as a parameter.

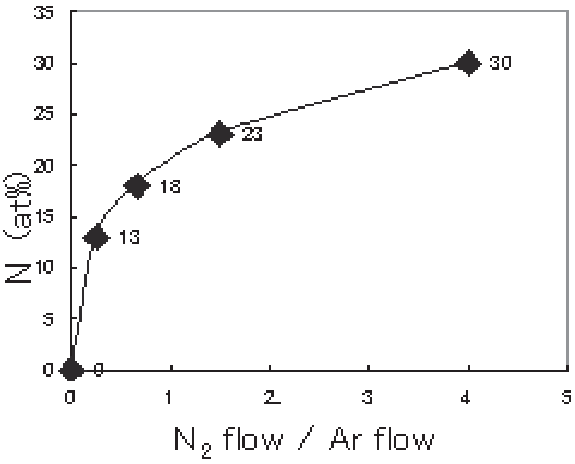

Figure 6 Nitrogen concentrations in the film vs. N_2/Ar flow rate

Table Ⅰ XPS measurement result

Sample	Flow / sccm			XPS / at %		
	N_2	Ar	CH_4	C1s	N1s	N/C
CN1	8.0	2.0	0	75	25	0.33
CN2			1.0	85	15	0.18
CN3			5.0	90	10	0.11
CN4			10.0	92	8	0.09

Table Ⅰ shows the XPS measurement result. It is seen that the ratio of N/C in the film decreases as the flow of CH_4 increases. This means that the C in CH_4 as well as the carbon target contributes to the growth of a-CNx.

Figure 7 shows the XPS N1s core-level spectra of a-CNx(H) films shown in Table Ⅰ. In order to investigate the bonding chemistry from N 1s spectra, each spectrum was decomposed into two peaks as shown in Fig.7. These peaks originate from C-N sp^3 bond (398.3eV) and C-N sp^2 bond (399.9eV).

Figure 8 shows the optical absorption data. The relationship between $(\alpha h\nu)^{1/2}$ and $h\nu$ are plotted in this figure. Here α, h and ν are absorption coefficient, Planck's constant and optical frequency, respectively. From these curves, we can obtain the Tauc energy gaps which corresponds to the $E_{LP\text{-}}\pi^*$ energy band in Fig.2.

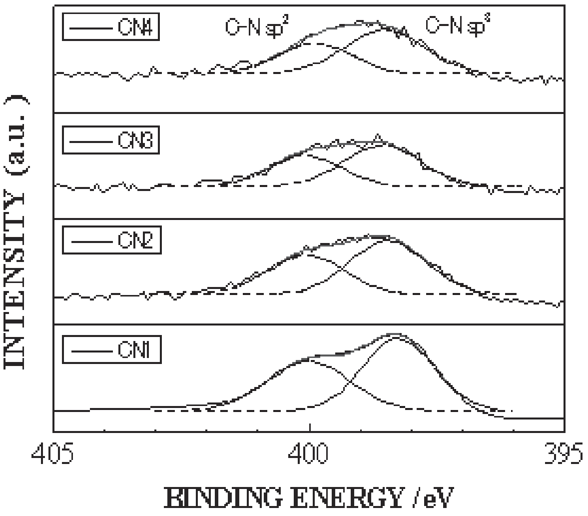

Figure 7 N 1s XPS spectra of a-CNx (H) films

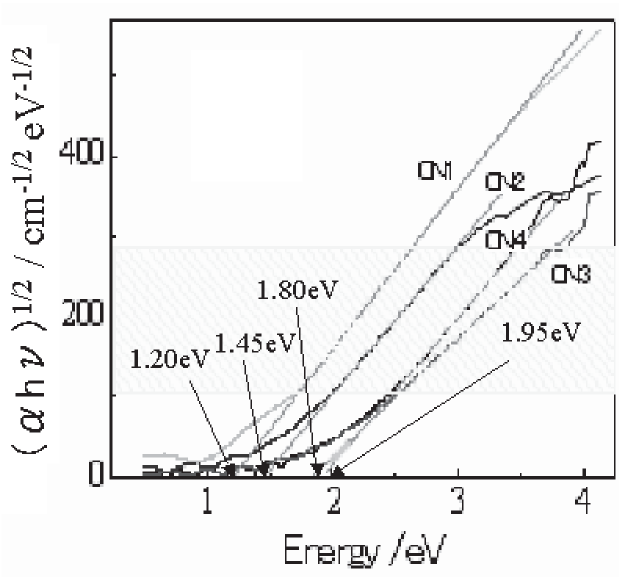

Figure 8 Optical absorption data

Table Ⅱ summarizes the results of Fig.7 and Fig.8. From this table, we understand that the ratio of C-N sp^3 increases as the ratio of N/C decreases and the increase of C-N sp^3 result in the increase of Tauc gap.

Figure 9 shows the C-N sp^2 fraction and optical energy gap Eg as a function of N/C ratio. It is well known that the C-N sp^2 phase clusters together and decrease the energy gap[4]. Therefore the smaller the N/C ratio, the smaller the C-N sp^2 clustering, which result in the increase of C-N sp^3 bond and energy gap.

Table Ⅱ Summary of decomposed two peaks

Sample	XPS / at %			
	N/C	C-N sp^2 %	C-N sp^3 %	E_0 eV
CN1	0.33	44.1	55.9	1.20
CN2	0.18	42.2	57.8	1.45
CN3	0.11	41.2	58.8	1.80
CN4	0.09	38.8	61.2	1.95

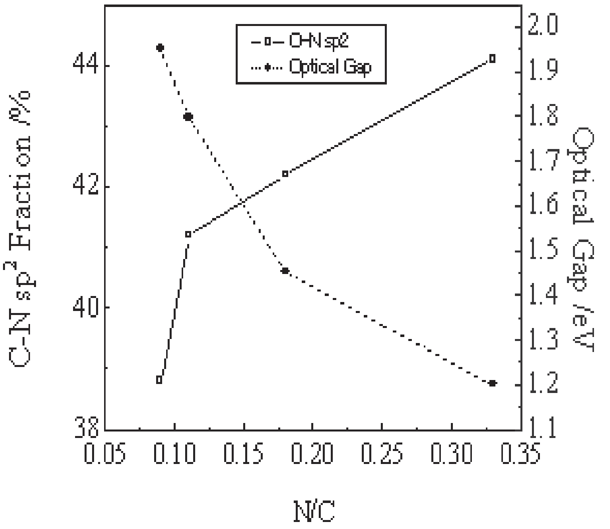

Figure 9 Relationship between N/C ratio and optical characteristics

Photo-Luminescence (PL) characteristic was investigated at room temperature by using Ar ion laser whose wavelength is 515nm. Figure 10 shows the PL result of Sample CN2 in Table Ⅰ.

As seen from this data, the longest wavelength is about 850nm (1.45eV), which corresponds to the tauc energy, and the peak wavelength is 590nm (2.1eV) corresponds to either π-π* transition or N_{LP}-σ* transition. On the other hand, PL result of sample CN1 that contains no H does not show the 590nm peak wavelength. From these results, the origin of 590nm red emission seems to be due to the radiation recombination through localized states relating C-H bonds.

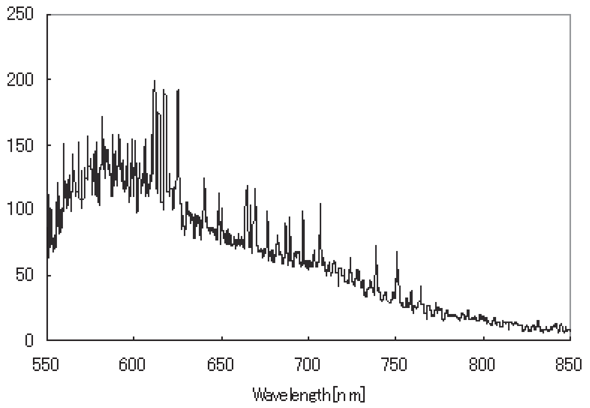

Figure 10 PL characteristics of a-CNx(H) composed by RF-sputtering

3. CONCLUSION

We fabricated a-CNx thin films aiming at white light emitting devices by using ECR-plasma CVD and RF-sputtering apparatuses. In order to envestigate the effect of hydrogen in CNx film, we used methane (CH_4) gas as the source or sub-source of carbon.

As a result of CL measurement of a-CNx that was composed by ECR-plasma-CVD, three peaks of 2.14eV, 2.56eV and 3.10eV were observed. The peak of 2.14eV is supposed to be due to the C-H bonds in the film.

As for the PL measurement of the samples, which were composed by RF-sputtering, 2.14eV (590nm) red peak was observed only in the sample which contain hydrogen in the films. From these two results, the origin of 2.1-2.14eV red peaks seems to be due to the radiation recombination through localized states relating C-H bonds.

Optical gap decreases as the N/C ratio increases, due to increase of C-N sp^2 content.

We can expect a-CNx as a white light emitting device by controlling content of C-N bonds and C-H bonds

REFERENCES

1) H. K. Jang, G. Kim, Y. S. Lee, S. W. Whangbo : J. Vac. Sci. Technol. A 17, 5 (1999) 2607.
2) W. J. Hsieh, P. S Shih, C. C. Liu, C. Y. Wang, H. C. Shil : Diamond. Relat. Mater. 14 (2005) 93.
3) R.Reyes, C. Legnani, P. M. Ribeiro Pinto, and M. Cremona : Appl. Phys. Lett. 82 (2003) 4017.
4) S.Nitta : Appl. Phys. 69. 7 (2000) 782.
5) A.C.Ferrari, S.E.Rodil, and J.Robertson : Phys. Rev. B67 (2003) 155306-1