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Photoluminescence characteristics of BN(C, H) prepared by chemical vapour deposition

MASAYUKI KAWAGUCHI, KOJI NOZAKI, YASUSHI KITA, MASAAKI DOI
Ube Research Centre, Central Glass Co. Ltd, Okiube, Ube 755, Japan

Hexagonal boron nitride (h-BN) containing carbon and hydrogen, BN(C, H), has been prepared by chemical vapour deposition. It shows wide photoluminescence in the range 300–600 nm. The luminescence is mostly bright and white-blue in colour to the naked eye. The peak position and shape of the luminescence spectra are totally different from those reported on BN(C, H) made by heating BN powder in a graphite crucible in the presence of hydrogen in the atmosphere. A study by electron spectroscopy for chemical analysis on BN(C, H) indicates that impurity carbon substitutes for nitrogen atoms in the h-BN crystal. In other words, impurity carbon can be introduced into h-BN as an acceptor.

1. Introduction

Since hexagonal boron nitride (h-BN) has a similar structure to graphite, it is expected that a composite can be prepared from both materials. The preparation of composite has actually been tried recently [1–4]. It is of interest to investigate not only the type of composite (mixture, hybrid, solid-solution or compound), but also the physical properties.

The luminescence from h-BN containing carbon and hydrogen as impurities (henceforth called BN(C, H)) has been reported [5, 6]. In these reports, since the doping of carbon into h-BN was performed spontaneously in the preparation process or by heating h-BN powder in a carbon crucible, the carbon content could not be controlled. The mechanism of luminescence has been proposed in these reports, but the defect levels which were introduced by doping with impurities of carbon, hydrogen and vacancy have not yet been established experimentally.

As the doping of impurities can be well controlled by chemical vapour deposition (CVD), BN(C, H) has been prepared by CVD in this report. We report the photoluminescence characteristics of BN(C, H). We also try to determine the electronic level of carbon centres by means of electron spectroscopy for chemical analysis (ESCA).

2. Experimental procedure

BN(C, H) was prepared by using the following gases: BCl_3 as a boron source; NH_3 for nitrogen; C_2H_2, C_2H_4 or C_3H_8 for carbon; and H_2 for hydrogen. Figs 1 and 2 show the CVD apparatus used in the present study. The preparation temperature was in the range 600–2000 °C.

In the temperature range between 600 and 1000 °C, BN(C, H) was deposited on a Ni substrate (width 20 mm, length 500 mm, thickness 3 mm) which was set in a hot-wall type of reactor (Fig. 1). The total gas pressure in the CVD furnace was 1.01×10^5 Pa. In the range between 1100 and 2000 °C, BN(C, H) was obtained on a graphite substrate (width 12 mm, length 40 mm, thickness 2 mm) which was directly heated by transmitting an electric current (Fig. 2). The total gas pressure in this case was 6.67×10^2 Pa.

Elementary analyses of carbon and hydrogen were carried out by the usual combustion method, using Pb_3O_4 as an oxidizing catalyst.

X-ray diffraction data were obtained by a diffractometer (Shimazu XD-5) with nickel-filtered CuK_α radiation. The scan speed was $1° \min^{-1}$.

Photoluminescence spectra were obtained by a spectrophotometer (Hitachi 650-10). The spectra calibrated by using a Rhodamine B solution were hardly different from the original ones.

ESCA was performed by a Shimazu ESCA 750 electron spectrometer with MgK_α radiation. Binding energies of elements were compensated by placing the C_{1s} peak of contaminating carbon, which was carried from the oil vapour of the high-vacuum pump, at 284.6 eV.

Resistivities of BN(C, H) films were measured by a two-probe d.c. method at room temperature.

3. Results and discussion

3.1. Appearance and carbon content of BN(C, H)

BN(C, H) as a creamy white film (thickness 50–500 μm) was obtained on the Ni substrate under adequate preparation conditions: for example, when the gas ratio of C_2H_2/NH_3 was 0.1 or less in a temperature between 600 and 1000 °C. A thin film (thickness < 200 μm) was translucent so that a letter under the film could be recognized. The carbon content of this film was less than 1 wt %, and the hydrogen content was less than 2 wt % (Table I).

BN(C, H) translucent thin film (thickness ~ 100 μm) was also obtained on the graphite substrate at a temperature between 1100 and 2000 °C.

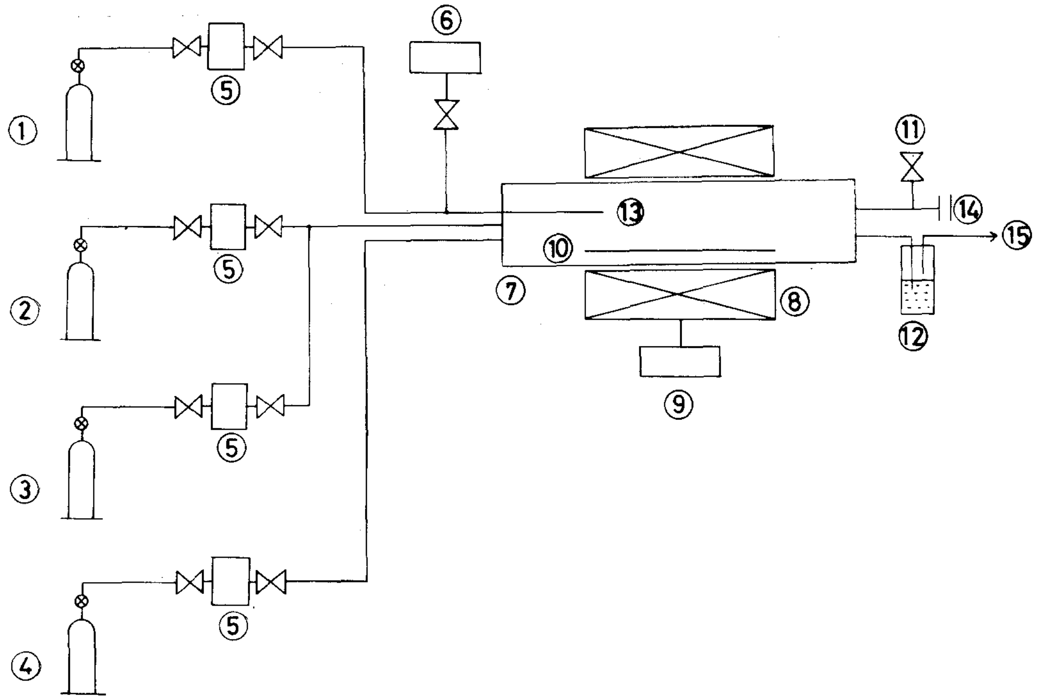

Figure 1 CVD apparatus for the preparation at lower temperatures (600–1000 °C): (1) BCl_3 bomb, (2) NH_3 bomb, (3) C_2H_2 bomb, (4) H_2 bomb, (5) mass flow controller, (6) pressure gauge, (7) quartz reaction tube, (8) electric furnace, (9) temperature controller, (10) Ni substrate, (11) outlet for gas analysis, (12) oil seal, (13) inlet tube for BCl_3, (14) rupture, (15) to scrubber.

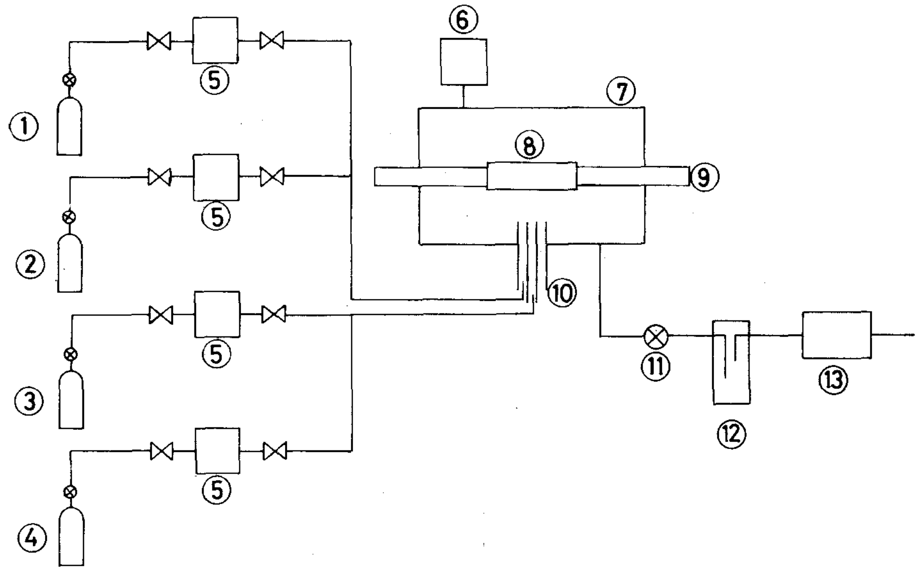

Figure 2 CVD apparatus for the preparation at higher temperatures (1100–2000 °C): (1) BCl_3 bomb, (2) H_2 bomb, (3) NH_3 bomb, (4) C_2H_4 or C_3H_8 bomb, (5) mass flow controller, (6) pressure gauge, (7) stainless steel reaction tube, (8) graphite substrate, (9) electrode, (10) gas inlet tube, (11) pressure controller bulb, (12) cold trap, (13) rotary pump.

Fig. 3 shows the relation between the C/N atomic ratio in source gases and the carbon content of BN(C, H) film prepared at 1800 °C. The carbon content did not increase in proportion to the C/N ratio below 1.0. However, it increased drastically with increasing C/N ratio above 1.5.

We considered, on the basis of these results, that BN(C, H) has a stable region in the small carbon content region ($0 < C < 2$ wt %). The hydrogen contents of these films were less than 2 wt %.

3.2. Crystal structure of BN(C, H)

Fig. 4 shows the X-ray diffraction pattern of the BN(C, H) creamy white powder which was prepared at 800 °C (No. 1 in Table I) and then reduced to powder by using an automatic grinder. Very broad 0 0 *l* and 1 0 diffraction lines were observed at similar positions to those of amorphous BN (a-BN) or carbon. This result means that the BN(C, H) prepared at lower temperatures has a similar structure to that of a-BN.

Fig. 5 shows the X-ray diffraction pattern of translucent film which was prepared at 1800 °C (No. 3 in Table I) and reduced to powder. 0 0 *l* diffraction lines are only observed at the same positions as those of h-BN, turbostratic BN (t-BN) or graphite. The *h k l* diffraction lines such as 1 0 0 or 1 0 1, however, were

TABLE I Carbon and hydrogen contents of BN(C, H) prepared at several temperatures

Sample No.	Preparation temperature (°C)	Carbon (wt %)	Hydrogen (wt %)
1	800	0.3_4	2.1_0
2	1000	0.1_0	1.5_4
3	1800	0.5_8	0.1_2
4	1800	0.1_0	
5	1800	0.2_5	0.4_0

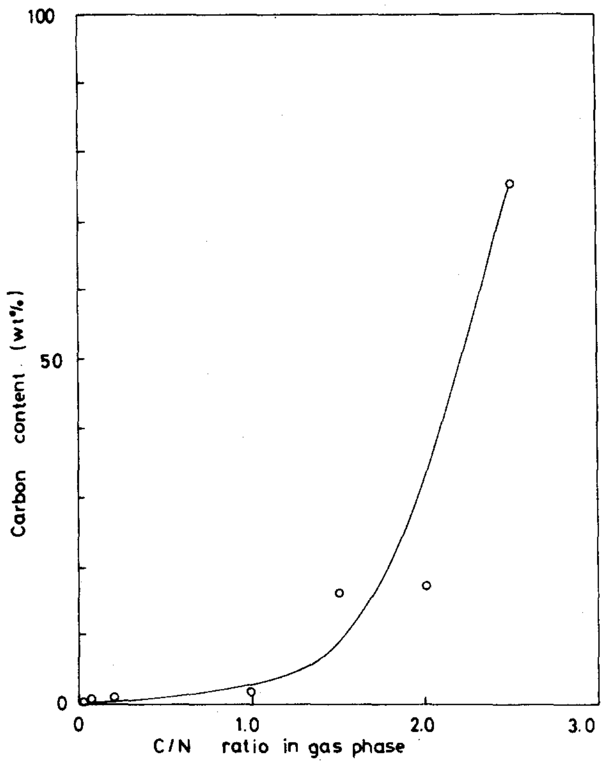

Figure 3 Relation between the C/N atomic ratio in source gas and the carbon content of BN(C, H) prepared at 1800 °C, 6.67 × 10^2 Pa.

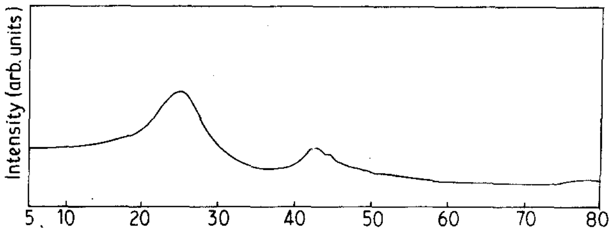

Figure 4 X-ray powder diffraction pattern of BN(C, H) prepared at 800 °C, 1.01 × 10^5 Pa.

too weak and broad to be observed clearly. These results indicate that the BN(C, H) prepared by CVD (CVD-BN(C, H)) at a higher temperature has a similar structure to that of t-BN whose orientational correlation between basal planes is disordered.

The half-width of the 0 0 2 diffraction line for CVD-BN(C, H) (1.3° in 2θ) was larger than that of BN(C, H) prepared by heating the BN powder at 1800 °C in a graphite crucible (HT-BN(C, H)) (0.5° in 2θ). This result means that CVD-BN(C, H) has a smaller and more heterogeneous crystallite size than HT-BN(C, H).

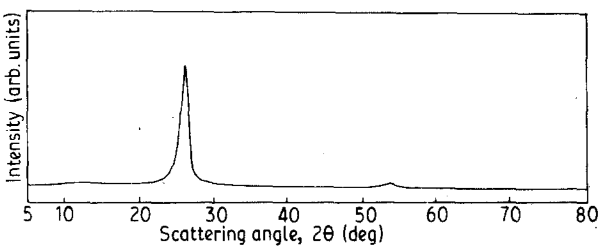

Figure 5 X-ray powder diffraction pattern of BN(C, H) prepared at 1800 °C, 6.67 × 10^2 Pa.

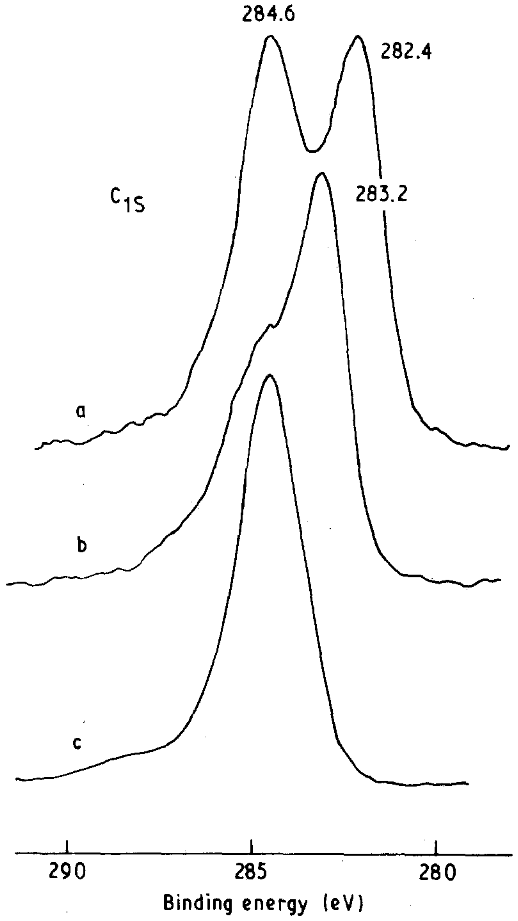

Figure 6 ESCA C_{1s} spectra for BN(C, H) prepared at 1800 °C, 6.67 × 10^2 Pa: carbon content (a) 0.1, (b) 0.25 and (c) 7 wt %.

3.3. Carbon centre defects in the BN(C, H) band

Fig. 6 shows ESCA C_{1s} spectra for the cleavage plane of BN(C, H) which were prepared at 1800 °C and had different carbon contents. Two split peaks were observed for the BN(C, H) which had 0.1 wt % carbon (Fig. 6a, No. 4 in Table I). A peak at a higher binding energy (284.6 eV) is due to contaminating carbon. The other at a lower binding energy (282.4 eV) is considered to be due to the carbon impurity in BN(C, H).

This result indicates that the carbon impurity in BN(C, H) is more negatively charged than the contaminating carbon or graphite. It can be interpreted as follows: the carbon impurity is surrounded by boron atoms whose electronegativity is smaller than that of carbon. In other words, the impurity carbon(IV) atom substitutes mainly for a nitrogen(V) atom in the h-BN crystal. It is, therefore, presumed that the carbon impurity is doped as an acceptor in h-BN.

The lower-energy peak shifted to a higher binding energy for the BN(C, H) containing 0.25 wt % carbon (Fig. 6b, No. 5 in Table I). The impurity carbon in this case is less negatively charged than that of BN(C, H) containing 0.1 wt % carbon. Only one peak (284.6 eV) was observed for BN(C, H) containing more than 1 wt % carbon (Fig. 6c).

These ESCA results suggest that the defect level of the carbon centre becomes shallower with an increase in carbon content of BN(C, H), because the interaction between impurity carbon atoms can increase with an increase in the carbon concentration. In fact, the specific resistivity of BN(C, H) decreased drastically with an increase in the carbon content within 1 wt % (Fig. 7).

3.4. Photoluminescence spectra of BN(C, H)

Fig. 8 shows the photoluminescence spectrum of BN(C, H) prepared at 1000 °C (No. 2 in Table I) on the Ni substrate by the CVD method (CVD-BN(C, H)). Light around 300 nm from a mercury lamp was most effective for exciting this material. The luminescence was observed in a wide range (300–500 nm) and had a peak at 343 nm. A white-blue colour could be seen by the naked eye.

Fig. 9 shows the photoluminescence spectrum of BN(C, H) prepared at 1800 °C (No. 4 in Table I) on a graphite substrate by the CVD method. Excitation light of 310 nm was employed in this case. The peak position also shifted to a longer wavelength than that of BN(C, H) prepared at 1000 °C. The peak positions of excitation and emission spectra generally showed a tendency to shift to longer wavelength with an increase in the preparation temperature, even for the same carbon content in BN(C, H). The peak shift suggests that the electronic structure of BN(C, H) changes with the preparation temperature.

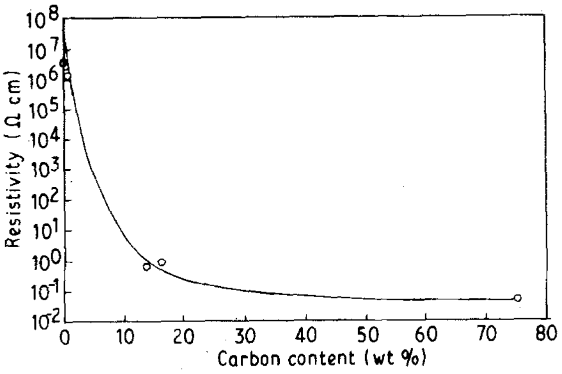

Figure 7 Resistivity of BN(C, H) film prepared at 1800 °C, 6.67 × 10^2 Pa.

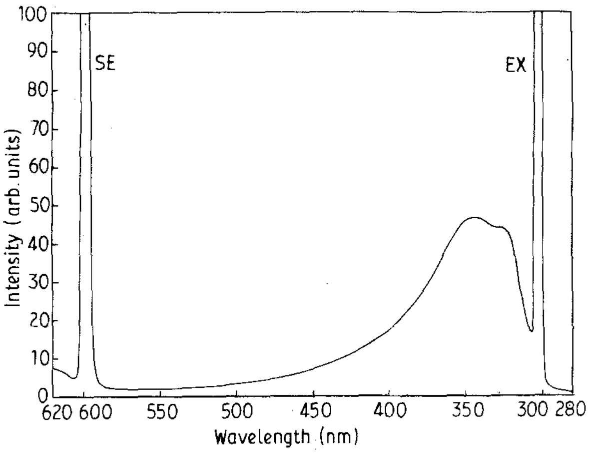

Figure 8 Photoluminescence spectrum of BN(C, H) prepared at 1000 °C, 1.01 × 10^5 Pa. EX indicates excitation light of 300 nm from the Hg lamp. SE indicates secondary light of 600 nm.

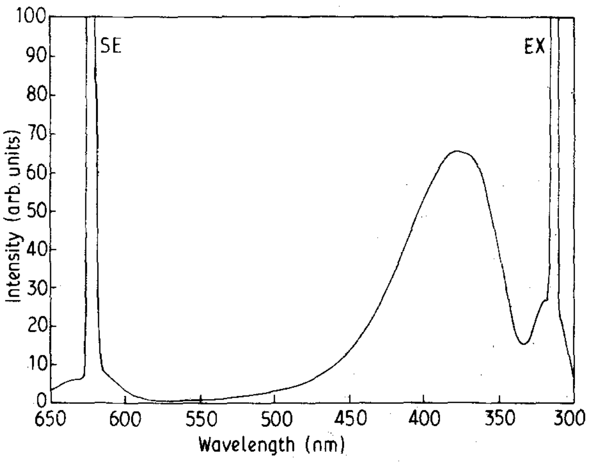

Figure 9 Photoluminescence spectrum of BN(C, H) prepared at 1800 °C, 6.67 × 10^2 Pa. EX and SE have the same meanings as in Fig. 8.

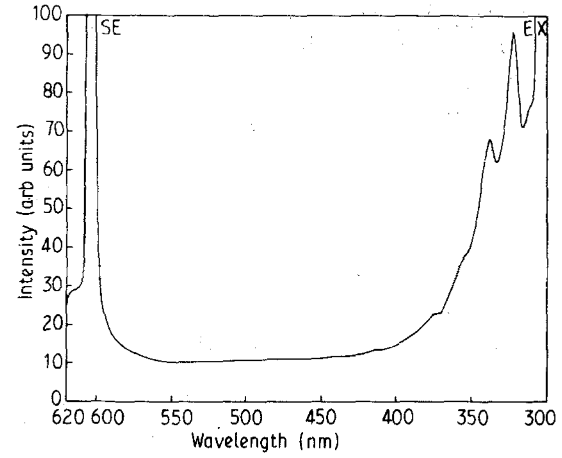

Figure 10 Photoluminescent spectrum of BN(C, H) prepared by heating BN powder at 1800 °C in a graphite crucible. EX and SE have the same meanings as in Fig. 8.

On the other hand, more than four split, sharp spectral lines were observed in the luminescence spectrum of the HT-BN(C, H) described in Section 3.2 (Fig. 10). The intensity was weaker than that of CVD-BN(C, H) described above.

3.5. Photoluminescence mechanism of BN(C, H)

The photoluminescence mechanism of BN(C, H) is considered to be as follows. The doping of carbon and hydrogen introduces defect levels in h-BN. In particular, the carbon impurity is mainly introduced at the acceptor level, as mentioned in Section 3.3. Excitation by ultraviolet light leads to electron transition between the levels and bands in BN(C, H), followed by the reverse electron transition, with the emission of light which has a lower energy than the excitation light.

It is considered that the sharp spectral lines in Fig. 10, which are similar to those of BN(C, H) described previously [6], are due to transitions between fewer defect levels and bands, because an equilibrium reaction occurs on heat treatment so that only fixed sites can be substituted. The band gap is also distinct in this case because of the homogeneous and larger crystalline size.

On the other hand, defect levels are distributed widely in CVD-BN(C, H), because the CVD reaction is a non-equilibrium one so that many sites can have an opportunity to be substituted. Also an indistinct band gap is created in this electronic structure because of the heterogeneous and smaller crystalline size. In fact, broader X-ray diffraction lines were observed for CVD-BN(C, H) than that of HT-BN(C, H), even at the same preparation temperature, as is mentioned in Section 3.2.

It is concluded that these differences in electronic structure lead to the quite different photoluminescent spectra of CVD-BN(C, H) and HT-BN(C, H).

3.6. Carbon content and luminescence intensity

Fig. 11 shows the relation between carbon content of BN(C, H) prepared at 1800 °C, 6.67×10^2 Pa, and intensity at the peak of the photoluminescence spectrum. The intensity tends to decrease with an increase in the carbon content. This result is explained by concentration quenching. Only very weak luminescence was observed at the carbon content of 1 wt %.

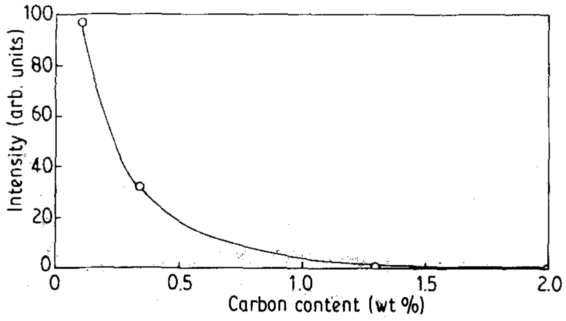

Figure 11 Relation between the carbon content of BN(C, H) and the intensity at the peak position of luminescence spectra.

4. Conclusions

1. BN(C, H) translucent thin film (<200 μm) has been deposited on Ni or graphite substrate at a temperature between 600 and 2000 °C by the CVD method.

2. The chemical shift of ESCA-C_{1s} spectra indicates that impurity carbon(IV) substitutes for nitrogen(V) in the BN crystal. In other words, the carbon can be introduced into h-BN as an acceptor.

3. Films of CVD-BN(C, H) show strong photoluminescence, having wide spectra in the range 300–600 nm.

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