

Electron Emission Property of Carbon Nanotubes Grown Using Different Source Gases

Jae-Hee Han, Tae Young Lee, Ji-Beom Yoo*, Chong-Yun Park

Department of Physics, Sungkyunkwan University, 300 Chunchun-Dong, Jangan-Gu, Suwon, 440-746, Korea

Taewon Jung, SeGi Yu, Whikun Yi and Jong Min Kim

NCRI Center for Electron Emission Source, Samsung Advanced Institute of Technology,
P.O.Box 111, Suwon 440-600, Korea

Abstract

Chemical species during growth of carbon nanotubes (CNTs) in direct current-plasma enhanced chemical vapor deposition were studied in details using C_3H_4 - NH_3 and CO - NH_3 mixtures through optical emission spectroscopy (OES). In the C_3H_4 - NH_3 system, the relative intensities of CN (388.3 nm) and CH (431.4 nm) decreased and that of C_2 (436 nm) increased, leading to sp^2 -graphitization into the CNT structure, leading to improvement of field emission property of CNTs. In the CO - NH_3 system, the trend is completely reversed. Attributing to the atomic oxygen for helping the graphitization of carbon, CNTs could be grown under the flow rate of CO (180 sccm)- NH_3 (10 sccm). Through these results, we suggest the growth mechanism in our system.

1. Introduction

Since the first discovery of carbon nanotubes (CNTs) in 1991 [1], tremendous excitement has been caused because of their excellent properties and potential application to various devices. Among various synthesis methods for the CNTs growth, chemical vapor deposition (CVD) method including plasma enhanced chemical vapor deposition (PECVD) has received much attention for the growth of CNTs because of its controllability and reliability in the synthesis of CNTs. Various source gas for the CNTs growth have been used including C_2H_2 , C_3H_4 , CH_4 , and CO , etc. In PECVD, especially, it has been considered that various active chemical species react with each other, forming sp^2 or sp^3 -hybridization materials of carbon. However, no study on identifying the chemical species for the CNTs growth in direct current (DC)-PECVD system has been reported up to now. Here we suggest the growth model of CNTs in

our PECVD through *in-situ* diagnosis of plasma during CNTs growth.

2. Experiments

In this work, the growth of vertically aligned CNTs was carried out using various source gases with NH_3 as a catalytic gas on two-catalyst metals (Co or Fe)-coated glass substrate with Cr buffer layers. The CNT growth was performed at the temperature around 550 °C by the PECVD. C_3H_4 , and CO gases were used as a carbon source and the NH_3 gas was used as a catalyst and a dilution gas, respectively. A DC plasma was used to grow vertically aligned CNTs. Detailed processes for the growth of CNTs were described in our previous report [2].

Optical emission spectroscopy (OES, SPEX 270N) was used to examine the species in the plasma during the CNTs growth process. The emission characteristics of CNTs were measured in a vacuum chamber with a parallel diode-type configuration at 5×10^{-7} mbar.

3. Results and Discussion

Figure 1 shows that OES spectra detected from the plasma of C_3H_4 or CO , and NH_3 gas mixtures for CNTs growth. In the plasma of the C_3H_4 - NH_3 gas mixture, CN and the atomic hydrogen (H_α) bands had a great portion of the whole, and the CH (431.4 nm) and C_2 (436.5 nm) band, which is the C_2 Swan system band with Q (4,2), also appeared. In case of the CO - NH_3 system, CN and CO radicals did.

In Fig. 2, for the C_3H_4 - NH_3 system, the relative intensities of monomeric CH and CN, and dimeric C_2 carbon species in the plasma are shown. The $I(CH)/I(H_\alpha)$ and $I(CN)/I(H_\alpha)$ decreased with the increase in NH_3 flow rate from 240 to 300 sccm, the

decay rate of the relative CN intensity was still larger than that of CH by a factor of 69. On the contrary, the intensity of C_2 (436.5 nm)/ H_α increased by a factor of 7. It has been known that the CN radical plays a role in the atomic hydrogen abstraction from the growing surface or gas phase forming the HCN species. In addition, because the CN species is produced at the expense of the atomic carbon and atomic nitrogen, a depleting of the atomic carbon has been caused. The reason for the decrease in the relative CN intensity with NH_3 addition can be attributed to the followings; i) for a given power (about 75 W) for sustaining plasma, the amount of the atomic nitrogen (did not detect from our OES result due to simultaneous strong bonding with other species) dissociated from plasma would not increase with NH_3 addition but decrease due to plasma quenching effect, resulting in the reduction of the amount of CN radical at the expense of both atomic carbon and nitrogen.

It has been shown that CH and C_2 are responsible for good diamond (C, sp^3 -hybridization) and graphite (C, sp^2 -hybridization) deposition, respectively [3]. This is consistent with the SEM data depicted in Fig. 3(a) and (b), which shows CNTs grown on Co catalyst metal-coated glass substrate using the mixture of C_3H_4 and NH_3 . As NH_3 flow rate increased from 240 to 300 sccm, the growth rate of CNTs increased, implying that sp^2 -graphitization into the CNT structure was facilitated by the increase in the amount of C_2 than CH radical in plasma of mixed gases of C_3H_4 and NH_3 . This result was also confirmed by Raman spectroscopy (not shown here).

For the CO- NH_3 system, as shown in Fig. 4, we found the condition for the CNTs growth on Fe-coated glass substrate at the ratio of CO (180 sccm) to NH_3 (10 sccm) flow rate, which are completely different from the C_3H_4 (300 sccm)- NH_3 (60 sccm) system. Therefore we performed the OES measurement over 5 to 26-sccm ranges of NH_3 flow rate. As shown in Fig. 4, the intensity of $I(CN)/I(H_\alpha)$ increased with NH_3 flow rate. It should be noted that the increment rate (by a factor of 41) in the relative ratio of CN to H_α with the increase in NH_3 flow rate from 5 to 10 sccm is much higher than that (a factor of 28) with the increase in NH_3 flow rate from 10 to 26 sccm. In the C_3H_4 - NH_3 system, because the amount of NH_3 (240 to 300 sccm) was higher than that of C_3H_4 (60 sccm), the effect of NH_3 addition did not significantly affect the relative intensity of CN to H_α . However, in the CO- NH_3 system, the amount of

NH_3 (5 to 26 sccm) was much smaller than that of CO (180 sccm), the relative intensity of CN to H_α was drastically changed with NH_3 flow rate, implying that the dissociation of NH_3 molecules into the atomic nitrogen and hydrogen is accelerated under its small fraction of the whole. Another notable fact is the increase in the relative intensity of CN to H_α with NH_3 addition. The tendency of bonding between the unsaturated atomic nitrogen dissociated from NH_3 plasma and the atomic carbon is very high (bonding enthalpy of C-N; 754.3 ± 10 kJ/mol), thus the amount of CN drastically increased with small NH_3 addition.

The intensity of $I(C_2; 436 \text{ nm})/I(H_\alpha)$ decreased with NH_3 addition as shown in Fig. 4. This is the opposite of the C_3H_4 - NH_3 system. The reason for this may be attributed to the more activated atomic nitrogen with NH_3 addition. The dissociated atomic nitrogen is strongly bonded to the atomic carbon and hydrogen. This is related to the increase in the relative intensity of CN as discussed above. However, the intensity of $I(CH; 389 \text{ nm})/I(H_\alpha)$ increased, indicating the increase in bonding reactions between the atomic hydrogen resulted from NH_3 addition and the atomic carbon from CO.

From the OES results stated above in the CO- NH_3 system, we found an interesting fact, which is the complete opposite tendency to the case in the C_3H_4 - NH_3 system. In the C_3H_4 - NH_3 system, the relative intensities of CN and CH decreased and that of C_2 increased with NH_3 addition. The other hands, in the CO- NH_3 system, the relative intensities of CN and CH increased, CO and C_2 decreased with NH_3 addition. Intriguingly, as shown in Fig. 3(d), CNTs were grown at the ratio of CO (180 sccm) to NH_3 (10 sccm) flow rate. To elucidate the CNTs growth under this condition, we observed another relative intensity of the species.

It is carefully noticed that the intensity of $I(O; 777.2 \text{ nm})/I(H_\alpha)$ (marked by both opened diamond and dashed-line) had a maximum value at the NH_3 flow rate of 10 sccm (indicated by dotted-arrow), as shown in Fig. 4, and the N_2 emission ranged from 337 nm to 405.9 nm linearly increased (not shown here). In our system, the production of NO radical is possible because the atomic nitrogen and oxygen can be generated from the NH_3 and CO plasma, respectively. Hong *et al.* reported that once NO was formed in the gas phase, a reaction of NO with active nitrogen species resulted in a significant

density of nitrogen atoms being present in the gas phase to engage in the "titration reaction" (a high-rate reaction): $N + NO \rightarrow N_2 + O$ [4]. Oxygen had several effects besides the increase in the atomic hydrogen concentration, such as acetylene reduction in the gas phase and graphitic carbon deposits on the growing film surface [5]. Even though the $I(C_2; 436 \text{ nm})/I(H_\alpha)$ decreased with NH_3 addition, CNTs could be grown at the NH_3 flow rate of 10 sccm due to such role of the atomic oxygen mentioned just above. Thus, we tentatively suggest that the maximum value of $I(O)/I(H_\alpha)$ at the NH_3 flow rate of 10 sccm may be responsible for the CNTs growth as depicted in Fig. 3(d).

Figure 5 shows the emission currents as a function of applied voltages ($I-V$) of CNTs with different source gases. The turn-on electric field, E_{to} , is defined as the electric field at the current density of $1 \mu A/cm^2$. The E_{to} of CNTs grown under the NH_3 flow rate of 240 sccm (see (i) of Fig. 5) and 300 sccm (see (ii) of Fig. 5) at the constant C_3H_4 flow rate of 60 sccm were $10.3 \text{ V}/\mu m$ and $6.1 \text{ V}/\mu m$, respectively, and that of CNTs under the flow rates of CO (180 sccm) and NH_3 (10 sccm) was $6.4 \text{ V}/\mu m$. The difference in the E_{to} values of CNTs grown using C_3H_4 with different NH_3 flow rates may be attributed to the difference in their average diameters, *i. e.* curvatures at the CNT tips, as shown in Fig. 3(a) and (b). On the basis of the results from OES and field emission analysis, we suggest that as the NH_3 flow rate increased at the constant C_3H_4 flow rate, C_2 radical, which is considered to be responsible for sp^2 -graphitization, increased in plasma, thus the growth of CNTs with smaller diameter was promoted, leading to improvement of the field emission property of CNTs.

It is noted that from the $I-V$ curve of CNTs grown using the mixture of CO (180 sccm) and NH_3 (10 sccm), shown in (iii) of Fig. 5, the onset of current density saturation (indicated by arrows) appeared at the relatively low value of $0.01 \mu A/cm^2$ at the electric field of $2.8 \text{ V}/\mu m$ and the rate of increase in the emission current decreased. However, in the CNTs grown using the mixture of C_3H_4 (60 sccm)- NH_3 (300 sccm) (see (ii) of Fig. 5), the current saturation occurred at higher current density value (about $6.4 \mu A/cm^2$). Thus, the E_{to} of CNTs grown using the mixture of CO- NH_3 was higher than that of CNTs using C_3H_4 - NH_3 even though the onset of the field emission from CNTs using the mixture of CO- NH_3 in

the low field region ($< 2.8 \text{ V}/\mu m$) was the smallest among the other CNTs.

4. Conclusion

In the C_3H_4 - NH_3 system, as the NH_3 flow rate increased from 240 to 300 sccm, the relative intensities of both $I(CN; 388.3 \text{ nm})/I(H_\alpha; 656.5 \text{ nm})$ and $I(CH; 431.4 \text{ nm})/I(H_\alpha)$ decreased. However, the relative intensity of $I(C_2; 436 \text{ nm})/I(H_\alpha)$ increased, giving rise to the sp^2 -graphitization into the CNT structure, leading to improvement of field emission property of CNTs. On the contrary, in the CO- NH_3 system, the relative intensities of $I(C_2)/I(H_\alpha)$ and $I(CO; 483 \text{ nm})/I(H_\alpha)$ decreased except the relative intensities of both $I(CN)/I(H_\alpha)$ and $I(CH; 389 \text{ nm})/I(H_\alpha)$. However, due to the atomic oxygen for helping the graphitization of carbon, CNTs could be grown at 10 sccm of NH_3 flow rate. The turn-on electric field, E_{to} , of CNTs using the mixture of CO- NH_3 was higher than that of CNTs using C_3H_4 - NH_3 .

5. Figures/Captions

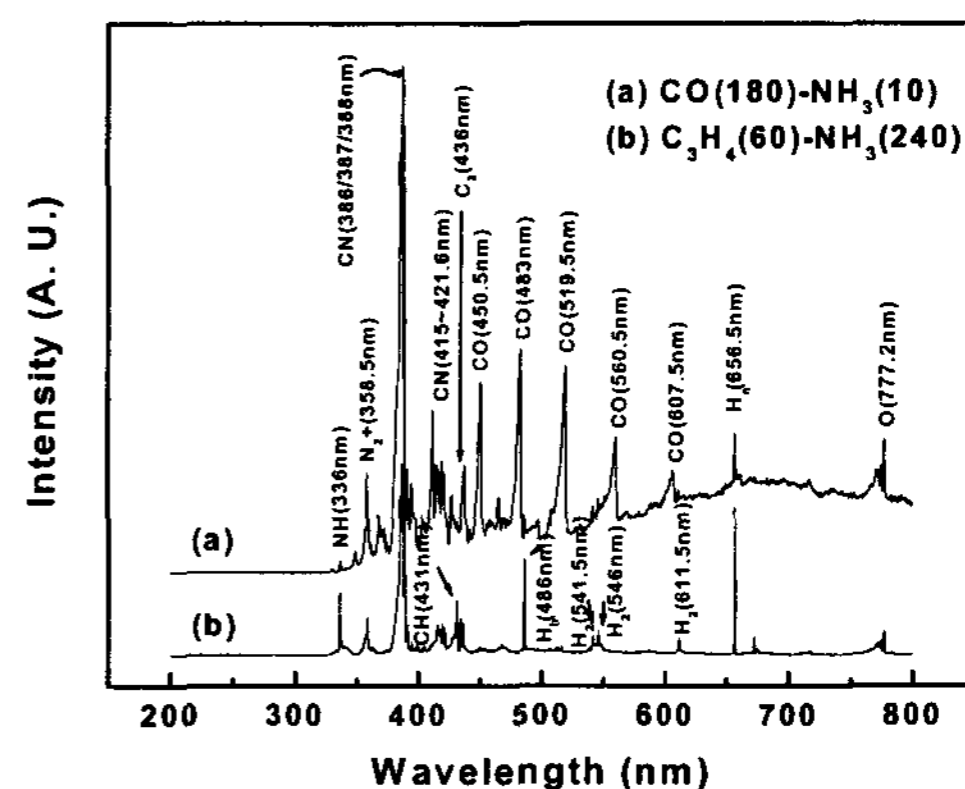


Fig. 1. OES spectra of CNTs grown using (a) the mixture of C_3H_4 and NH_3 and (b) CO and NH_3 .

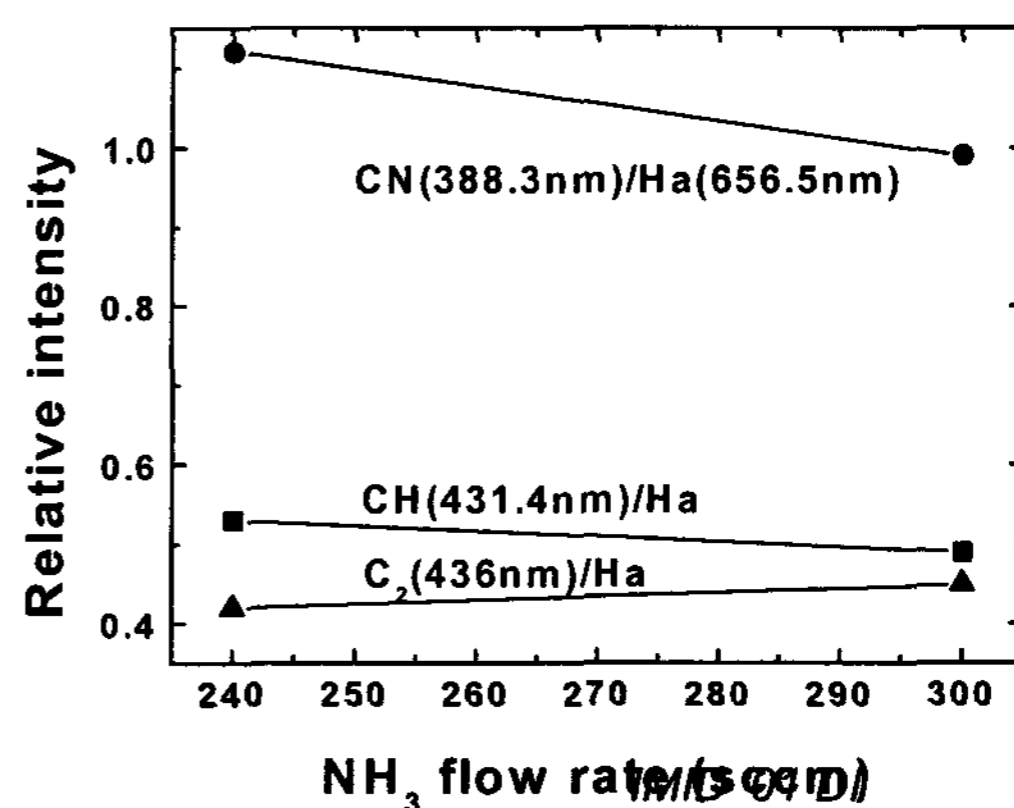


Fig. 2. Relative intensities of various chemical species such as CN, CH, and C₂.

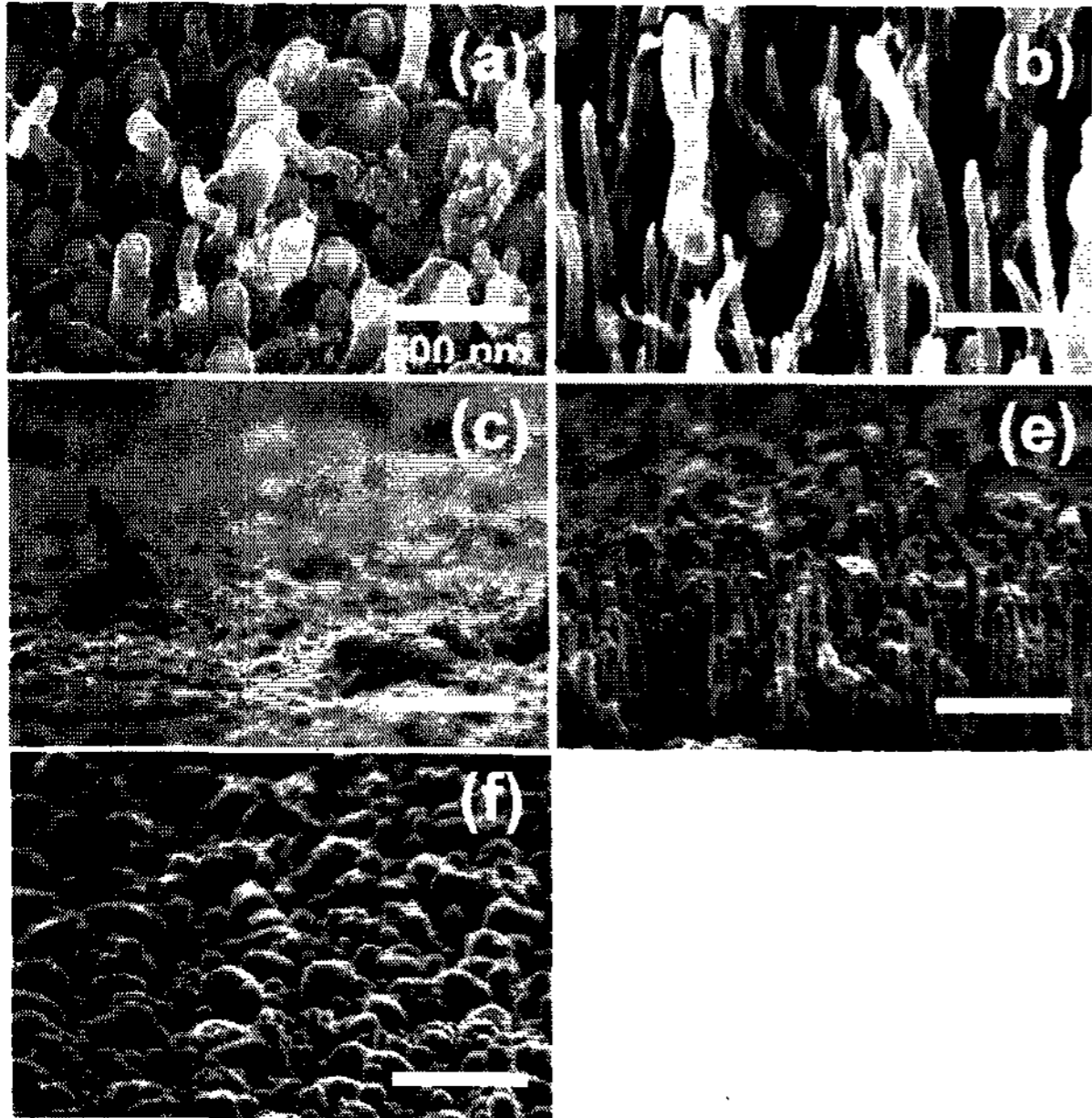


Fig. 3. SEM images showing the morphology of CNTs using various source gases: (a) C₃H₄ (60 sccm)-NH₃ (240 sccm), (b) C₃H₄ (60 sccm)-NH₃ (300 sccm), (c) CO (180 sccm)-NH₃ (5 sccm), (d) CO (180 sccm)-NH₃ (10 sccm), (e) CO (180 sccm)-NH₃ (26 sccm). Scale bars indicate 500 nm equally.

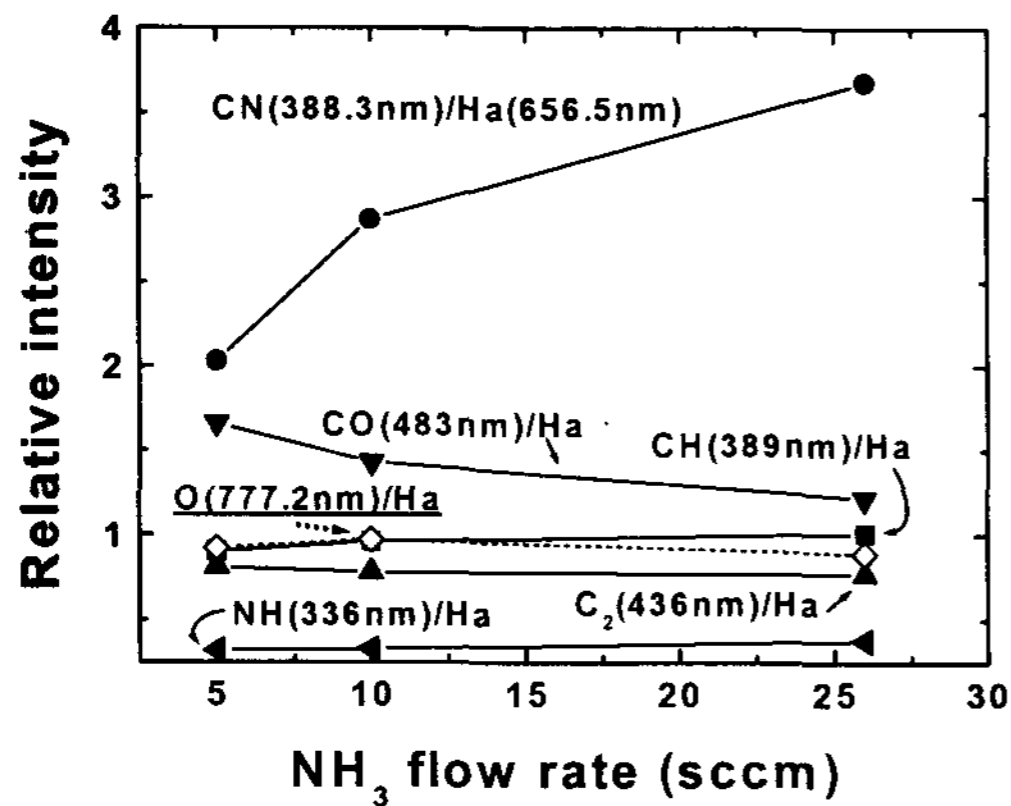


Fig. 4. Relative intensities of various chemical species such as CN, CH, C₂, CO, and O.

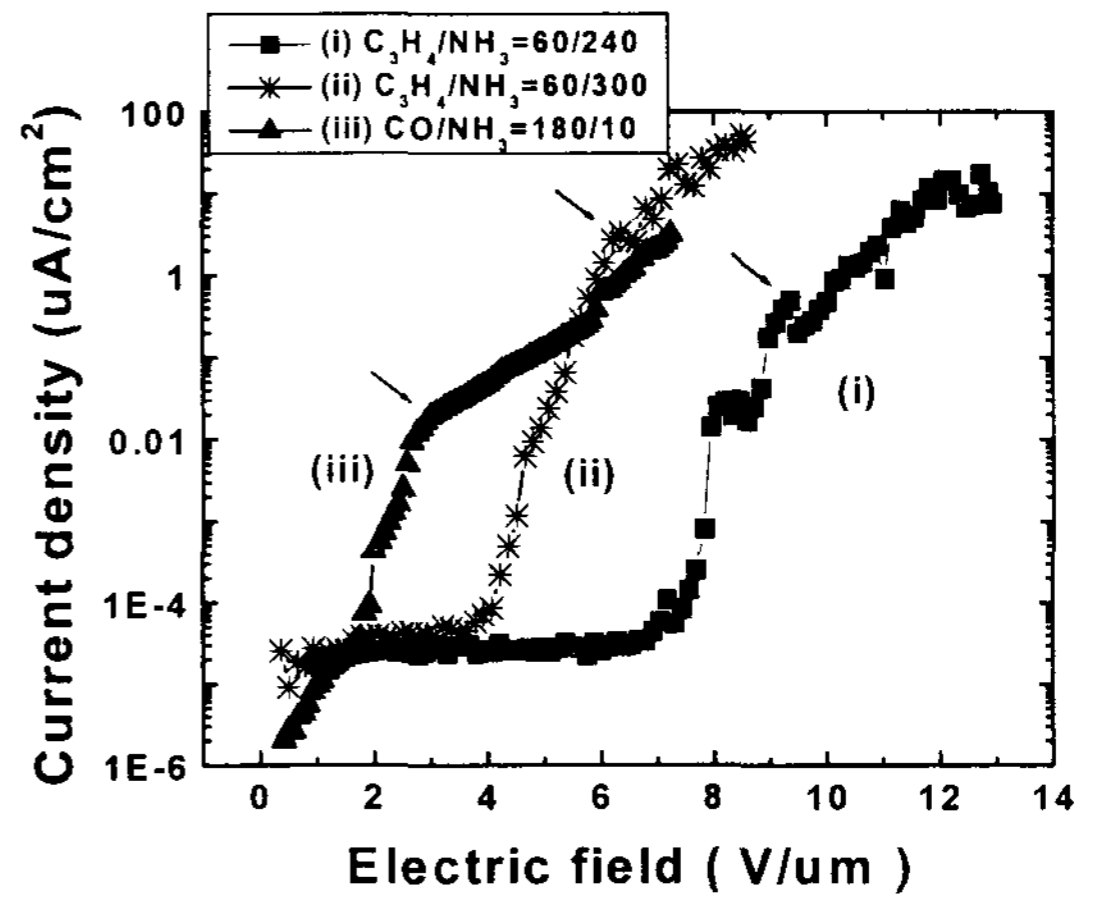


Fig. 5. Current vs. applied electric field (*I-V*) curves with different source gases and the NH₃ flow rate. Current saturations are indicated by arrows.

6. Acknowledgements

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6. References

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