Hydrogenated Amorphous Carbon Nitride Films with Controlled Hydrogen Densities—Application to Electric Field Emission Devices

Haruhiko Ito*, Yukihisa Kogure, Satoshi Oki and Hidetoshi Saitoh

Department of Chemistry, Nagaoka University of Technology,
Kamitomioka, Nagaoka, Niigata 940-2188, Japan

(Received 23 August 2006; accepted 26 September 2006)

Key words: amorphous carbon nitride, ECRCVD, ZnO:Al whisker, electric field emission

Hydrogenated amorphous carbon nitride films which presumably include oxygen atoms (a-CN\textsubscript{x}:(O):H) were prepared by the electron cyclotron resonance (ECR) plasma chemical vapor deposition (CVD) of mixed gases of He, BrCN, and H\textsubscript{2}O. The partial pressures of He and BrCN were 3 and 2 mTorr, respectively. The relative number density of the hydrogen atoms was varied by controlling the partial pressure of H\textsubscript{2}O (P\textsubscript{H\textsubscript{2}O}) in the range of 0.0–0.6 mTorr. The films were coated by ECRCVD onto Al-doped ZnO (ZnO:Al) single crystal whiskers, which were prepared by atmospheric CVD with the reactants of Zn(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{2} and Al(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{3} to manufacture cold cathode devices. The I-V characteristics of the devices were confirmed to be the Fowler-Nordheim type, and the work functions were determined to be 4.7±0.4, 2.3±0.1, 2.0±0.1, and 1.9±0.1 eV under the conditions of P\textsubscript{H\textsubscript{2}O} values of 0.0, 0.2, 0.4, and 0.6 mTorr, respectively.

1. Introduction

Amorphous carbon nitrides (a-CN\textsubscript{x}) and hydrogenated a-CN\textsubscript{x} (a-CN\textsubscript{x}:H) are promising owing to their important properties of, for example, mechanical hardness\textsuperscript{1–4} and electric field emission.\textsuperscript{5–8} Recent studies of the electric field emission from a-CN\textsubscript{x} have suggested the importance of the N atoms for obtaining a low threshold electric field and a high current density of the emitted electrons.\textsuperscript{5–8} The phenomenon of electric field emission is based on the so-called Fowler-Nordheim (F-N) tunneling effect whereby electrons tunnel through a potential barrier in the presence of an electric field.\textsuperscript{19} The original F-N theory assumed that

\*Corresponding author: e-mail: bu7dd8@nagaokaut.ac.jp
the electrons are ejected from a flat surface. Later, this theory was extended so that electrons are ejected from a sharp tip where the magnitude of the electric field is enhanced, resulting in the low threshold and high current density of the emitted electrons.\(^{(10)}\) The enhanced electric field around the tip region is phenomenologically expressed as \(\beta E\), where \(E [\text{Vm}^{-1}]\) is the applied electric field and \(\beta\) is the geometric enhancement factor. Saitoh and coworkers have developed a novel method of manufacturing electric field emission devices where \(a\text{-CN}_x:H\) thin films are coated onto Al-doped ZnO (ZnO:Al) single crystal whiskers.\(^{(11–14)}\) They found that the work functions for the \(a\text{-CN}_x:H\) materials are in the range of 0.64–3.81 eV, where, in particular, a low threshold voltage can be attained when \(a\text{-CN}_x:H\) contains NH or OH terminations having large dipole moments.\(^{(11)}\) They concluded that the device has a profound character that combines a low \(\phi\) and large \(\beta\), resulting in the low threshold voltage necessary for electron emission.

The above findings indicate the importance of the hydrogen content of the films. As discussed in many reports on the connection between the structure and the properties of the \(a\text{-CN}_x\) films, it is necessary to synthesize the films under the condition that the hydrogen-containing materials such as \(\text{H}_2\text{O}\) should be eliminated as much as possible to obtain mechanical hardness.\(^{(1–4)}\) The reason for the necessity of excluding \(\text{H}_2\text{O}\) molecules is that they are the parents of the hydrogen-termination structure of the films that prohibits the development of the three-dimensional network structure. On the contrary, hydrogen-containing molecules should be included in the starting materials to generate the electric field emission properties, according to previous studies.\(^{(11–14)}\) The \(a\text{-CN}_x:H\) films, which are synthesized under the condition that the hydrogen-containing molecules are included in the reaction system, are, in general, mechanically soft. Therefore, the reaction design to attain the electric field emission properties should be distinguished from that for the mechanical hardness.

Previous discussions on the connection between the structure of \(a\text{-CN}_x:H\) and the electric field emission properties have been limited to the two extreme cases where the hydrogen atoms are either included or not included. The intermediate case, i.e., the dependence of the field emission properties on the hydrogen content of \(a\text{-CN}_x:H\), has not been taken into consideration. To investigate this dependence, the following experiments are made in the present study. First, a reaction system was established which was able to control the hydrogen content of the films, and the structural analysis of the films was carried out. Second, the \(a\text{-CN}_x:H\) films with controlled hydrogen content were coated onto the ZnO:Al single crystal whiskers, and the field emission properties were studied.

In the previous studies, \(a\text{-CN}_x:H\) films were prepared using a microwave (MW) plasma CVD system where the CN radicals produced by the decomposition of BrCN by the MW discharge flow of Ar deposit onto the substrate.\(^{(11–14)}\) The typical pressure of Ar was 0.1 Torr. The source of the hydrogen atoms of the films in that reaction system was the \(\text{H}_2\text{O}\) molecules included in the starting materials and/or adsorbed on the wall of the apparatus. The partial pressure of \(\text{H}_2\text{O}\) was thought to be negligible compared with that of Ar but could not be measured accurately. Therefore, the hydrogen content of the films in that system was uncontrollable. To control the hydrogen content of the films, it is necessary to use a reaction system in which the uncontrollable \(\text{H}_2\text{O}\) molecules are excluded as much as possible and the \(\text{H}_2\text{O}\) molecules are introduced externally in a controlled fashion. One of the suitable systems
for realizing such a reaction design is the electron cyclotron resonance (ECR) plasma CVD, where the films can be formed under a low-pressure condition (typically of the order of mTorr). Under such a condition, the partial pressure of H₂O can be monitored accurately, so that the hydrogen content of the films may be controllable. In our preliminary experiment, the ECR plasma of the mixed gases of Ar, BrCN, and H₂O was studied, but the resulting films were easy to peel off the substrate; when He was used instead of Ar, such a problem did not occur. Therefore, an ECR plasma of an mixed gases of He, BrCN, and H₂O was used in this study.

2. Experimental Procedure

2.1 ECR-plasma CVD apparatus

Figure 1 shows a schematic of the ECR-plasma CVD apparatus used in the present study. It consists of a stainless-steel chamber with an inner diameter of 90 mm and an ECR discharge source (Irie Koken RBG-152L) which are evacuated to 10⁻⁵ Torr using turbomolecular (80 L/s) and oil-rotary (180 L/min) pumps. Microwaves (2.45 GHz, 70 W) are introduced into the discharge section through a coaxial cable and an antenna. An external magnetic field is applied using permanent magnets arranged in the vicinity of the upper part of the ECR-discharge source, where electrons are trapped and accelerated resonantly around the magnetic field of 875 G perpendicular to the electric field of the microwaves. A stainless-steel nozzle with an inner diameter of 1 mm is set downstream of the discharge section from which reactants are introduced. A substrate holder (60 mm in diameter) insulated from the wall of the chamber was set 5 mm downstream of the nozzle tip. Pressure was monitored using an ionization gauge, which was set downstream of the substrate holder.

Fig. 1. ECRCVD apparatus used in this study.
The experiment was carried out using the following procedure. After the reaction chamber was evacuated sufficiently, He (99.999%) was introduced into the discharge section through a needle valve along with a desiccant (P₂O₅). H₂O molecules adsorbed on the substrate surface and the wall of the chamber were removed by discharging He for 1.5 h. They were confirmed to be fully removed by observing the OH(A2Π−X2Σ⁺) emission spectrum, which was completely diminished. After the desiccation procedure, BrCN (Nacalai Tesque, quoted purity of 95%) was passed through a Teflon needle valve and P₂O₅, and was introduced into the chamber through a stainless-steel nozzle with an inner diameter of 1 mm. Finally, H₂O was admixed into the flow of BrCN from another nozzle. The pressures of He and BrCN were fixed at \( P_{\text{He}} = 3 \) mTorr and \( P_{\text{BrCN}} = 2 \) mTorr, respectively, and were monitored inside the chamber. The pressure of H₂O, \( P_{\text{H}_2\text{O}} \), was varied in the range of 0.0–0.6 mTorr; under the condition of \( P_{\text{H}_2\text{O}} > 0.6 \) mTorr, the plasma was not turned on. The discharged products were deposited on the Si substrate or the ZnO:Al whiskers, the latter of which were formed as described in §2.3.

### 2.2 Analysis of films

According to the method of preparation of films described in §2.1, films obtained under the condition of adding H₂O may contain oxygen atoms, and therefore be suitable to be denoted as \( \text{a-CN}_{x}:(\text{O}):\text{H} \). They were deposited onto the Si substrates with the deposition time of 45 min. A part of the substrate was masked by aluminum foil to measure the film thickness by observing the cross-sectional view using scanning electron microscopy (SEM; JEOL, JSM6700F). The film thicknesses were 130, 108, 85, and 67 nm under the conditions of \( P_{\text{H}_2\text{O}} = 0.0, 0.2, 0.4, \) and \( 0.6 \) mTorr, respectively.

The structural analysis of the sample was performed using a Fourier transform infrared (FTIR) spectrophotometer (Nicolet IMPACT-410) and a Raman spectrometer (Renishaw, System2000). IR spectra were measured in the right AEM-main mode with a MCT/A detector and a resolution of 4 cm⁻¹. Raman spectra were obtained in the backscattering mode using an Ar⁺ laser operating at a wavelength of 514.5 nm and a power of 2 mW. The wavelength resolution was held at 1 cm⁻¹, and the spatial resolution was ≤1 μm. The scattering signal was detected using a CCD detector.

Compositional analysis was made for films deposited directly onto the substrate holder. Films were peeled from the holder, and flakelike powder was used for the compositional analysis of organic materials (Yanako CHN Corder MT-5), by which the atomic percents of the C, N, and H atoms are obtained.

### 2.3 Preparation of \( \text{a-CN}_{x}:(\text{O}):\text{H}/\text{ZnO:Al} \) cold cathode whiskers

ZnO:Al whiskers were prepared using the atmospheric CVD apparatus reported previously.\(^{16–18}\) The reactants, \( \text{Zn(C}_2\text{H}_7\text{O}_2)_2 \) (Soekawa Chemical Co., quoted purity of 99.9%, 8.0 g) and \( \text{Al(C}_2\text{H}_7\text{O}_2)_3 \) (Soekawa Chemical Co., quoted purity of 99.9%, 0.5 g), were vaporized at a temperature of 115°C, which was measured using a K-type thermocouple. The gas-phase reactants were carried by desiccated nitrogen gas flowing at a rate of 1.2 L/min and then sprayed from the metallic nozzle directly onto the single-crystalline n-type silicon (Shin-etsu Semiconductor Co., resistivity of 2.00–50.0 Ωcm) substrate mounted on an electric heater. The temperature of the heater was 520°C, measured using the K-type
thermocouple, at which the reactants decomposed thermally to form whiskers. The distance between the nozzle and the substrate was maintained at 15 mm throughout the experiments. The deposition time was 3 h. A typical Al concentration in the whisker was 0.8 at.%. The lengths of whiskers were 30–40 μm, according to the SEM observations.

On the ZnO:Al whiskers prepared above, the a-CNᵸ:(O):H films were deposited using the same ECR-plasma CVD apparatus described in §2.1. The deposition times were set to be 30, 45, 75, and 75 min under the conditions of \( P_{\text{H}_2\text{O}} = 0.0, 0.2, 0.4, \) and 0.6 mTorr, respectively, so that the thickness of the a-CNᵸ:(O):H films was 50–100 nm. Before and after coating the a-CNᵸ:(O):H films, the surface morphologies of the resulting materials were observed by SEM.

2.4 Measurement of I-V characteristic

Field emission devices were manufactured from the cold cathode of a-CNᵸ:(O):H/ZnO:Al whiskers and an anode made of a quartz substrate coated successively by an ITO thin film (100 nm in thickness) and an Eu-doped Y₂O₃ (Y₂O₃:Eu) phosphor. Using a thin glass spacer, the cathode and the anode were separated so that the spacing between the whisker tip and the anode surface was 300 μm. After the baking process (100°C, 24 h), the I-V characteristics of the devices were measured at a pressure of \(<10^{-8}\) Torr using a digital multimeter.

3. Results and Discussion

3.1 Film characterization

3.1.1 IR spectra

Figure 2 shows the IR spectra of films deposited under the conditions of \( P_{\text{H}_2\text{O}} \) values of (a) 0.0, (b) 0.2, (c) 0.4, and (d) 0.6 mTorr. The intensities of the IR spectra shown in Fig. 2 are normalized by their film thickness. All the films show the C=N stretching vibration at 2300 cm⁻¹ and the G- and D-bands around 1550 and 1350 cm⁻¹, respectively. The appearance of the G- and D-bands in the IR spectra originates from the breakdown of the center symmetry of the hexagonal rings of the graphitic structure by the substitution of N atoms. In addition, the C=C olefinic and C-C vibrations may overlap the G- and D-bands. The intensities of the C=N stretching, G- and D-bands were observed to be nearly independent of \( P_{\text{H}_2\text{O}} \). In addition to these bands, the antisymmetric stretching vibrations of CO₂ and H₂O were observed around 2500 cm⁻¹ and in the range of 3700–4000 cm⁻¹, respectively, the origins of which may be atmospheric. Apart from these common features, the NH₃ (\( γ = 1, 2 \)) or OH stretching vibrations in the range of 3000–3600 cm⁻¹ showed the following features. As shown in Fig. 2(a), the intensity of these vibrations was negligibly weak; this observation indicates that the desiccation using \( P_2\text{O}_5 \) is effective in removing the H₂O contamination. As shown in Figs. 2(b)–(d), the intensity of these vibrations depends on \( P_{\text{H}_2\text{O}} \). Hence, the origin of the above hydrogen termination structure is the H₂O molecules introduced externally in a controllable fashion. From the above IR observations, the film prepared under the condition of \( P_{\text{H}_2\text{O}} = 0.0 \) mTorr may be classified as a-CNᵸ, whereas the films prepared under \( P_{\text{H}_2\text{O}} = 0.2–0.6 \) mTorr may be classified as a-CNᵸ:(O):H.
3.1.2 Raman spectra

Figure 3 shows the Raman scattering spectra of the films prepared under the conditions of $P_{H_2O}$ values of (a) 0.0, (b) 0.2, (c) 0.4, and (d) 0.6 mTorr. All the spectra show an inclination of the baseline toward the high wavenumber region. These baselines are due to the fluorescence from the conjugated structure of the carbon network, and characteristic to carbon-related materials with low mechanical hardness. As shown in Fig. 3(a), the G- and D-bands were observed around 1550 cm$^{-1}$ and 1360 cm$^{-1}$, respectively. This observation indicates that the present $a$-CN$_x$ film has a graphitic structure whose network size may be of the order of nanometers. On the other hand, these bands disappear when H$_2$O molecules are introduced, as shown in Figs. 3(b)--3(d). This observation indicates that the development of the graphitic network structure is suppressed by the formation of the hydrogen termination structures.

3.1.3 Compositional analysis

Table 1 lists the results of the compositional analysis of the $a$-CN$_x$:(O):H materials prepared under the conditions of $P_{H_2O}$=0.0, 0.2, and 0.6 mTorr, where the atomic percents of the H, C, and N atoms are shown. According to the results listed in this table, the atomic percents of H atoms seem to be nearly independent of $P_{H_2O}$; even under the condition of $P_{H_2O}$=0.0 mTorr, films contain H atoms. These observations seem to be inconsistent with the IR spectra shown in Fig. 2. Since the $a$-CN$_x$:(O):H materials have the tendency to absorb H$_2$O molecules under atmospheric pressure, the H atoms of atmospheric origin may be incorporated into the film during the waiting time of several days between the film preparation and the compositional analysis. Therefore, the number of H atoms may be overestimated, because the H atoms of both atmospheric and sample origins may be...
analyzed simultaneously. Since the measurements of the IR spectra were made just after the deposition, the H atoms detected may originate predominantly from the chemisorbed H atoms.

3.2 Work functions for a-CNx:(O):H/ZnO:Al cold cathodes

3.2.1 Geometric factors

The work functions for a-CNx:(O):H/ZnO:Al cold cathodes were determined from the Fowler-Nordheim (F-N) analysis described below. According to the F-N theory, the current density, \( J \) [Am\(^{-2}\)], is expressed as

\[
J = A \frac{F^2}{\phi} \exp \left( -B \frac{\phi^{3/2}}{F} \right),
\]

Fig. 3. Raman spectra of a-CNx:(O):H films.

<table>
<thead>
<tr>
<th>( P_{\text{H}_2\text{O}} ) [mTorr]</th>
<th>H [at.%]</th>
<th>C [at.%]</th>
<th>N [at.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>37.4</td>
<td>36.6</td>
<td>26.0</td>
</tr>
<tr>
<td>0.2</td>
<td>38.2</td>
<td>34.8</td>
<td>27.0</td>
</tr>
<tr>
<td>0.6</td>
<td>36.8</td>
<td>32.2</td>
<td>31.0</td>
</tr>
</tbody>
</table>

Table 1
Compositional analysis of a-CNx:(O):H.
where $\phi$ is the work function [eV], and $A$ and $B$ are constants having the following values

$$A = 1.54 \times 10^{-6}$$

and

$$B = 6.87 \times 10^{-9},$$

and $F (= \beta E)$ is the electric field strength applied to the tip of the whisker cold cathode. $\beta$ is represented by the radius of curvature $\rho$ of the whisker tip and the distance between electrodes, $d$, as

$$\beta = \frac{2d}{\rho \ln \frac{2d}{\rho}},$$

assuming that only one tip contributes to the field emission. To evaluate $\rho$, a parabolic equation,

$$y = ax^2 + bx,$$

is applied to the SEM image of the cold cathode, from which $\rho$ is evaluated as

$$\rho = \left| \frac{(1 + b^2)^{3/2}}{0.5a} \right|. $$

Figure 4 shows the SEM images of the cold cathode formed under the conditions of $P_{\text{H}_2\text{O}}$ values of (a) 0.0, (b) 0.2, (c) 0.4, and (d) 0.6 mTorr. These images were fitted to eq. (5), from which $\rho$ and $\beta$ are obtained according to eqs. (4) and (6), as listed in Table 2.

### 3.2.2 I-V characteristics

Figure 5 shows the I-V characteristics of the $a$-CN$_x$:H/ZnO:Al cold cathodes formed under the conditions of $P_{\text{H}_2\text{O}}$ values of (a) 0.0, (b) 0.2, (c) 0.4, and (d) 0.6 mTorr. The voltages for each sample that are required to obtain an electric current density of 2 $\mu$A are (a) 2.75, (b) 1.99, (c) 2.48, and (d) 1.73 kV. From this observation and the result described in §3.1.1, this current has a negative dependence on the density of hydrogen termination structures in the $a$-CN$_x$:H film; the high voltage value observed in (c) is due to a large $\rho$ in this sample (see Table 2). Figure 6 shows F-N plots of the $a$-CN$_x$:H/ZnO:Al cold cathodes prepared under the conditions of $P_{\text{H}_2\text{O}}$ values of (a) 0.0, (b) 0.2, (c) 0.4, and (d) 0.6 mTorr. All the plots show a linear dependence of $\log (I/V^2)$ on 1000/V, where $I$ and $V$ are in units of A and V, respectively. Hence, the electron-emission characteristic is confirmed to be F-N type. The
inclinations of these dependencies correspond to $\beta/\phi^{3/2}$, from which the $\phi$ values are evaluated, as listed in the last column of Table 2 in units of eV. $\phi$ under $P_{\text{H}_2\text{O}}=0.0$ mTorr was (4.7±0.4) eV; this value is almost the same as that for pure (uncoated) ZnO:Al whiskers, 4.6 eV.\(^{(11,12)}\) The predominant termination structure of $a$-CN\(_x\):(O):H/ZnO:Al cold cathode may be the C≡N (nitrile) group; this group has a negligible contribution to the lowering of $\phi$. $\phi$ under $P_{\text{H}_2\text{O}}=0.2$ mTorr is (2.3±0.1) eV, which is 2.4 eV lower than that under $P_{\text{H}_2\text{O}}=0.0$ mTorr. Therefore, it is confirmed that the introduction of even a small number of water molecules into the reaction system causes a large decrease in the work function. $\phi$ decreases further toward 1.9±0.1 eV under $P_{\text{H}_2\text{O}}=0.6$ mTorr.

Table 2
Analysis of geometric factors and work functions of $a$-CN\(_x\):(O):H/ZnO:Al cold cathode.

<table>
<thead>
<tr>
<th>$P_{\text{H}_2\text{O}}$ [mTorr]</th>
<th>$\rho$ [nm]</th>
<th>$\beta \times 10^{-2}$</th>
<th>$\phi$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>85.0±1.0</td>
<td>8.4±0.2</td>
<td>4.7±0.4</td>
</tr>
<tr>
<td>0.2</td>
<td>150.0±3.0</td>
<td>4.5±0.1</td>
<td>2.3±0.1</td>
</tr>
<tr>
<td>0.4</td>
<td>180.0±5.0</td>
<td>4.1±0.1</td>
<td>2.0±0.1</td>
</tr>
<tr>
<td>0.6</td>
<td>120.0±3.0</td>
<td>5.9±0.2</td>
<td>1.9±0.1</td>
</tr>
</tbody>
</table>

Fig. 4. SEM images of tips of $a$-CN\(_x\):(O):H/ZnO:Al cold cathodes.
Figure 7 shows a photograph of the luminescence from $Y_2O_3$:Eu phosphor, which is excited by the electrons generated from the electric field emission from the $\alpha$-CN$_x$:O:H/ZnO:Al cold cathode prepared under the condition of $P_{H_2O}=0.4$ mTorr. This photograph indicates the potential of the $\alpha$-CN$_x$:O:H/ZnO:Al cold cathode as an electric field emission device.
4. Conclusion

\( a\)-\( CN_x:(O):H \) films were prepared by the ECR plasma CVD of mixed gases of He, BrCN, and H\(_2\)O as the starting materials. It was confirmed that the relative number density of the NH or OH terminations which appear in the range of 3000–3600 cm\(^{-1}\) of the IR spectra were controlled by varying \( P_{H_2O} \). Electric field emission devices were fabricated by coating the \( a\)-\( CN_x:(O):H \) films onto ZnO:Al single crystal whiskers, and the \( I-V \) characteristics of these devices were measured. The \( \phi \) values were determined to be from 4.7±0.4 to 1.9±0.1 eV as \( P_{H_2O} \) increases from 0.0 to 0.6 mTorr. This observation indicates that the work function of the \( a\)-\( CN_x:(O):H \) films is strongly dependent on the relative number density of the NH or OH termination structures and that it is preferable to incorporate these terminations as much as possible to fabricate electric field emission devices with a low work function.

Acknowledgements

The authors are grateful to Professors Ikuzo Nishiguchi and Hirofumi Maekawa for their kind provision to use their apparatus for the compositional analysis. Shin-ya Takano is acknowledged for his technical assistance in the observation of the IR and Raman spectra. Tsukasa Washio is also acknowledged for his technical help in the early stage of this work. This work was supported by a Grant-in-Aid for Scientific Research, from the Ministry of Education, Culture, Sports, Science and Technology, under Contract No. 16040208.
References