

Chemical vapor deposition of a-CN_x:H films for electron field emission using band supermagnetron plasma

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Abstract. A supermagnetron plasma apparatus with two band magnetron cathodes, which can form uniform magnetron plasma under a stationary magnetic field (about 160 G), was used to deposit a-CN_x:H films at N₂ gas concentrations of 0 and 70%. A high deposition rate of about 85±5 nm/min was obtained at a low dc self-bias voltage, between -20 and -62 V. The optical band gap could be controlled between 1.1 and 3.8 eV. The double-layer a-CN_x:H films with optical band gaps of 2.2 eV (upper layer; N₂ 0%) and 1.5 eV (lower layer; N₂ 70%) formed on p-Si substrate showed a low-threshold-emission electric field of 9 V/μm.

1. Introduction

The excellent electron transport characteristics of amorphous carbon films have attracted considerable attention due to their promising applicability to cold-cathode materials in the next generation of high-performance electronic devices, such as display devices and microelectronics [1-3]. Hydrogenated amorphous carbon (a-C:H) and hydrogenated amorphous carbon nitride (a-CN_x:H) films are of considerable interest due to their unique properties such as a high degree of hardness, low stress and chemical inertness [4]. Carbon nanotubes are also the recent leading candidate for use as field emitters [5, 6]. However, they must be deposited at high temperatures of 700–1000°C, which is too high to deposit on low-cost glass substrates [6, 7]. a-CN_x:H films can be deposited at temperatures below about 400°C [8, 9], and show excellent electron field emission characteristics from their flat surfaces [2, 10-12]. For cold cathode operation of devices such as flat-panel displays and panel light sources, a large-area electron emission with a low working voltage is required. Recent studies have shown that the field-emission behavior of a-CN_x:H planar structures is largely influenced by many factors relating to electron transport, such as the sp²/sp³ bonding ratio, surface morphology, and CC, CN, and CH bonding configurations. Many efforts have been made to reveal the relationship between field emission characteristics and preparation methods [11-14].

In the preparation of a-CN_x:H films by plasma chemical vapor deposition (CVD), high-speed and low-temperature deposition is preferable. For a high deposition rate, high-density plasma such as supermagnetron plasma (up to an order of 10¹¹ cm⁻³) is preferable [15, 16]. The supermagnetron plasma becomes very dense at an rf phase difference of 180°, which is suited to uniform deposition by rotating a magnetic field parallel to the cathode or by using a band-type magnetron cathode under a stationary magnetic field [17]. Using these plasma CVD apparatuses, the high-rate and uniform deposition of a-CN_x:H films can be achieved.

The addition of N atoms to a-C:H films, i.e. a-CN_x:H films, supports a lower electrical resistivity and a narrower optical band gap [15]. This could be caused by the increase in the sp²/sp³ ratio, the



increase in the sp^2 cluster size or the connection of sp^2 clusters by N atoms [13, 18]. The emission threshold field is reported to be dependent on the distribution of sp^2 clusters. It gives rise to the high internal field enhancement within a- CN_x :H films [12]. Using supermagnetron plasma apparatuses, a- CN_x :H layers with low resistivity and/or high N atom concentration have been realized [14, 19]. These layers render excellent field emission characteristics [8].

In this study, a- CN_x :H films were prepared using $i-C_4H_{10}$ as a hydrocarbon source and N_2 as the mixing gas. At the upper and lower electrode rf powers (UPRF/LORF) of 50–500/50–500 W (UPRF = LORF), $i-C_4H_{10}$ /(none or N_2) mixed gas was used for the deposition of the a-C:H or a- CN_x :H planar structures. The factors relating to electron transport, such as the size or number of CC sp^2 clusters and a three-dimensional configuration of sp^3 CC bonds of these a- CN_x :H films, were controlled by the choice of rf powers and N_2 gas ratios, respectively. The field emission characteristics of these layers with single- or double-layer structure were evaluated and the mixing effect of N_2 gas was evaluated.

2. Experimental procedure

a- CN_x :H films were formed using the band supermagnetron plasma CVD apparatus shown in Figure 1. Two cathodes were arranged in parallel. The shape of each cathode was an electrode with rounded side surface, like a pillow [20]. By generating electron $E \times B$ drift with a closed loop over the front and back surface of the magnetron cathode, a uniform magnetron plasma was easily formed over the front surface of the magnetron cathode, i.e. the band magnetron cathode. By placing these two cathodes face-to-face in parallel at an electrode spacing of 30 mm, uniform supermagnetron plasma was generated over the cathode, as shown in the figure. The size of each flat cathode front surface was about 110×110 mm in square. Two different rf power sources with the same rf frequency (13.56 MHz) were supplied to two electrodes inserted into a grounded metal chamber. The front surface of the upper electrode was covered with a graphite plate to avoid the contamination of wafers by sputtering from upper metal electrode. The phase difference between the two rf voltages was controlled to be approximately 180° using a phase shifter, and a stationary magnetic field of approximately 160 G was applied parallel to the two electrode surfaces. The lower electrode (substrate holder) was heated to 30°C . Isobutane ($i-C_4H_{10}$; 15 sccm)/ N_2 (0 or 35 sccm) was used as a deposition gas, and the gas pressure was controlled to be 4 Pa. The film thicknesses were measured by profilometry (ULVAC DECTAK-3). Using optical absorption data measured with a UV/vis/NIR spectrometer (Shimadzu

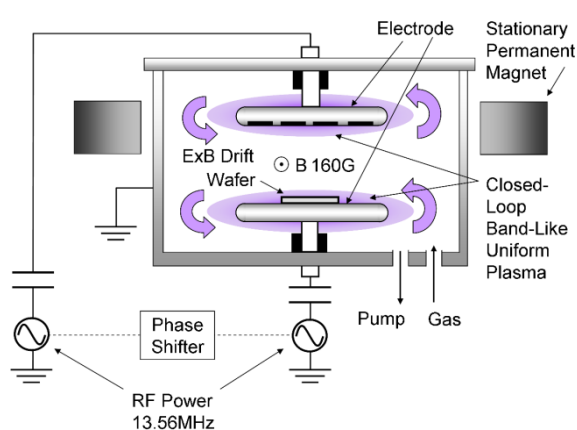


Figure 1. Schematic of the band supermagnetron plasma CVD apparatus with a stationary permanent magnet.

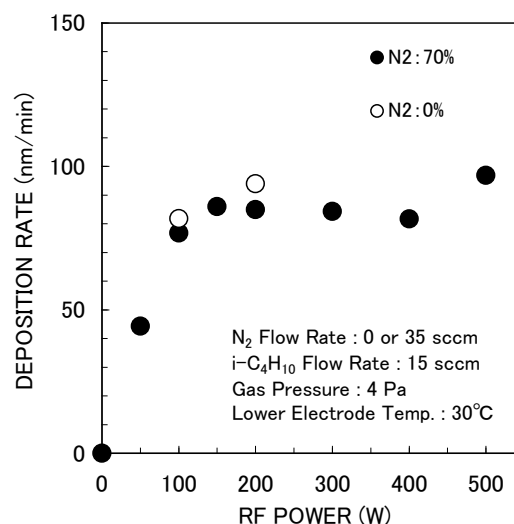


Figure 2. Deposition rate of a- CN_x :H films (N_2 of 0 or 70%) measured as a function of rf power (UPRF/LORF, UPRF = LORF).

UV-3100PC), the optical band gap was estimated from the Tauc plot based on the relation $(\alpha E)^{1/2} = A(E - E_G)$, where A is a constant, α is the absorption coefficient, E is the photon energy, and E_G is the optical band gap [21]. The bonding configurations of a-CN_x:H were measured using a Fourier transform infrared (FTIR) spectrometer (JIR WINSPEC-50). The thickness of the a-CN_x:H film used in FTIR analysis was controlled to be about 450 nm for all the samples.

3. Results and Discussion

The deposition rate of the a-CN_x:H films was measured as a function of rf power (UPRF = LORF), as shown in Figure 2. The deposition rate increased with rf power from 0 to 150 W. With the further increase of rf power from 150 to 500 W, the deposition rate changed little and was about 85±5 nm/min. At all rf powers, the nitrogen gas mixture had little influence on the deposition rate. From this experiment, it seems that the deposition rate increased with the increase of rf power from 0 to 150 W. With the further increase of rf power from 150 to 500 W, the formed a-CN_x:H films would be sputter-etched by positive ions generated in the plasma, and the deposition rate would increase very little. To investigate the sputter effect of this high-density plasma, the dc self-bias voltage (V_{DC}) of the lower electrode was measured, as shown in Figure 3. The absolute value of V_{DC} increased monotonously from 0 to -131 V with the increase of rf power from 0 to 500 W. The increase of the absolute value of V_{DC} from -41 to -131 V would cause high sputter-etching of deposited a-CN_x:H films.

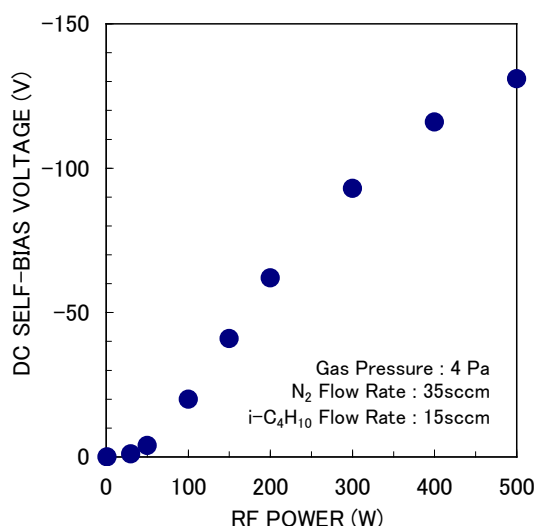


Figure 3. V_{DC} of lower electrode measured as a function of rf power.

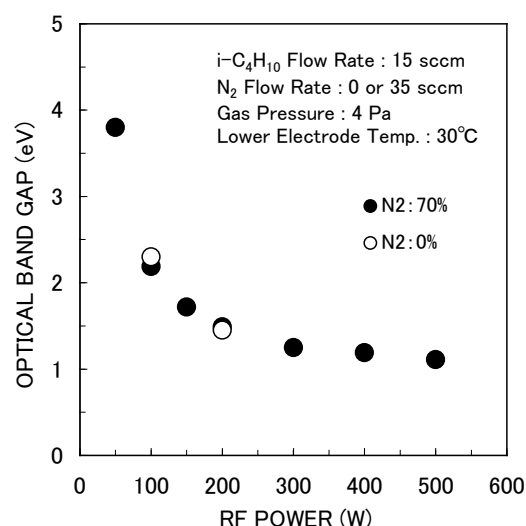


Figure 4. Optical band gap of a-CN_x:H films (N₂ of 0 or 70%) measured as a function of rf power.

The optical band gap of a-CN_x:H films was measured as a function of rf power, as shown in Figure 4. It decreased from 3.8 to 1.1 eV with the increase of rf power from 50 to 500 W, independent of the N₂ gas concentration (0 or 70%). This large decrease of the optical band gap was caused by the large increase of V_{DC} , i.e., ion bombardment energy. With the increase of ion bombardment energy, the size or number of CC sp² clusters would be increased [13].

The hardness of a-CN_x:H films was measured as a function of rf power, as shown in Figure 5. Hardness increased largely from 10 to about 24 GPa with the increase of rf power from 50 to 200 W. The hardness of a-C:H films was measured at 100 and 200 W, and was higher than that of a-CN_x:H films (N₂ gas concentration of 70%). Between the rf power of 200 to 500 W, that of a-CN_x:H films was almost constant (23±1 GPa). These values were slightly higher than that of vitreous silica (SiO₂),

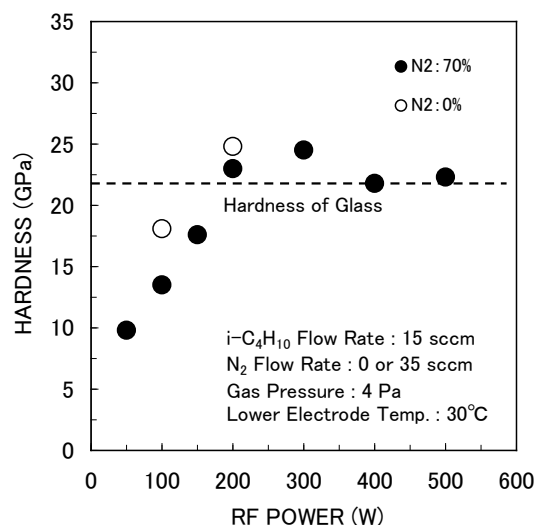


Figure 5. Hardness of a-CN_x:H films (N₂ of 0 or 70%) measured as a function of rf power.

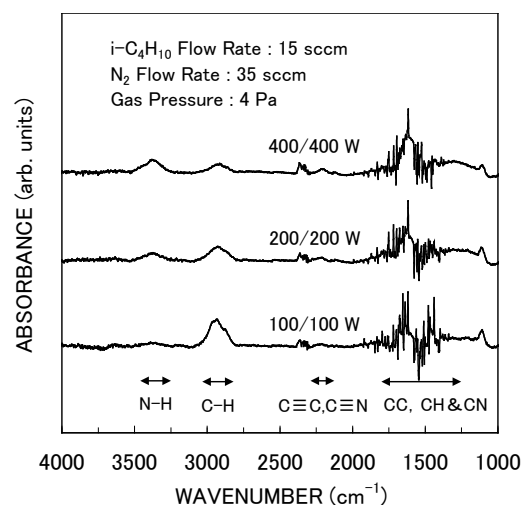


Figure 6. FTIR absorption spectra of a-CN_x:H films (N₂ of 70%) measured as a function of rf power.

which we measured as 22 GPa. Such a high hardness was ascribed by the inclusion of a three-dimensional configuration of sp³ CC bonds and also sp² CC bonds. In spite of such a low V_{DC}, between -60 (200 W) and -130 V (500 W), high hardness was achieved using this uniform band supermagnetron plasma CVD apparatus. This plasma CVD apparatus is suited to synthesizing hard a-CN_x:H films under very low V_{DC} (< -130 V).

FTIR absorption spectra were measured for a-CN_x:H films deposited at rf powers of 100, 200 and 400 W, as shown in Figure 6. The intensities of the absorption bands at 3300 cm⁻¹ (NH bonds) increased with rf power. This increase in intensity was caused by the inclusion of nitrogen atoms in the films [22]. The intensities of absorption bands at 2930 cm⁻¹ (CH₃, CH₂, and CH bonds) were decreased with the increase in rf power. Those at 1100 to 1700 cm⁻¹ (C=C, C=N, and C=N-H bonds) increased slightly with rf power. The FTIR absorption spectrum of a-C:H (100 or 200 W) was also measured, and was similar to that of a-CN_x:H film deposited at 100 W. In the spectrum, no peaks at 1100 to 1700 cm⁻¹ (C=C, C=N, and C=N-H bonds) were observed.

a-CN_x:H films of about 200-nm thickness with single- or double-layer structures were deposited at an rf power of 100–500 W on p-Si substrates to investigate the influence of the rf power and layer structure on their field emission characteristics, as shown in Figures 7 and 8. The surface morphology of the 200-nm thick a-CN_x:H film with single-layer structure (N₂ of 70%, 500 W) deposited for field emission measurement was analyzed by AFM. The surface of the a-CN_x:H film was flat with a surface roughness less than 1 nm over an area of 500 × 500 nm² or 5 × 5 μm², as shown in Figure 9 [23]. In the case of the double-layer structure, the layer thickness of each a-CN_x:H film (N₂ of 0 or 70%) was about 100 nm. Fowler-Nordheim (FN) plots of their field emission characteristics and the constructions of the field emitters are shown in the figure insets. The threshold emission electric field (E_{TH}) was defined as the applied electric field at the field emission current of 0.01 μA. In the case of single-layer structure (N₂ of 70%), the minimum E_{TH} of 13 V/μm was obtained at rf powers of 200, 300 and 400 W, and the maximum E_{TH} 17 V/μm was obtained at an rf power of 500 W. This means that the fitting between the two energy levels of a-CN_x:H and p-Si is important to ensure the flow of electrons from p-Si to a-CN_x:H layer, i.e., electrons in the valence band of p-Si (0.01 Ω cm; about 1 × 10¹⁹ cm⁻³) are injected into the conduction band (including CC sp² clusters) of a-CN_x:H by tunneling with a high electric field applied between p-Si and n-type a-CN_x:H [24]. The electron channel formed

in a-CN_x:H film may be CC sp² clusters. The optimal rf powers in this experiment for the energy level fitting were 200, 300 and 400 W. In the case of the double-layer structure [upper layer (N₂ of 0 and 70%), 100 W; lower layer (N₂ of 70%), 200 W], E_{TH} took small values of 9 and 12 V/μm, respectively. The FN plots of these a-CN_x:H thin films with single- and double-layer structures were almost linear, as shown in the figure insets. This means that the electron field emissions examined obeyed the FN relationship for field emission. From this experiment, it was found that a double-layer structure with wide optical band gap (upper layer) is effective to lessen E_{TH}.

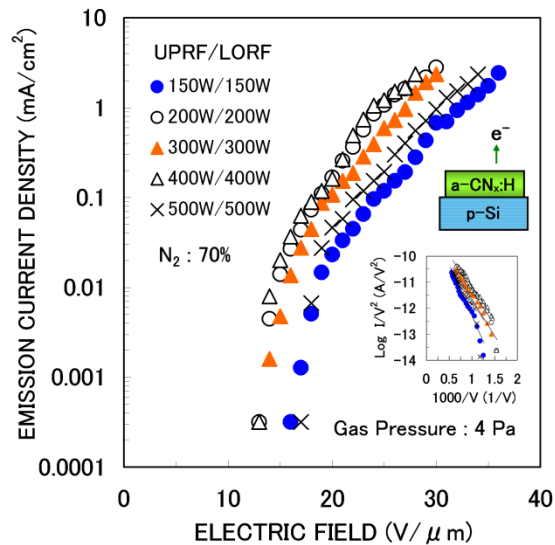


Figure 7. Emission current-voltage characteristics of a-CN_x:H films (single-layer) as a function of rf power. The inset shows their FN plots and their constructions.

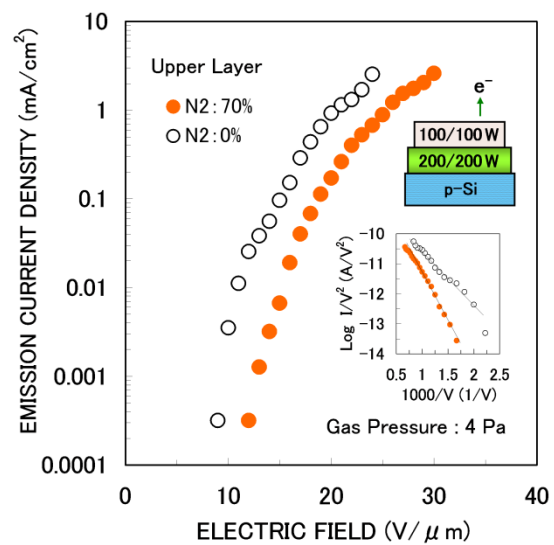


Figure 8. Emission current-voltage characteristics of a-CN_x:H films (double-layer) as a function of rf power. The inset shows their FN plots and their constructions.

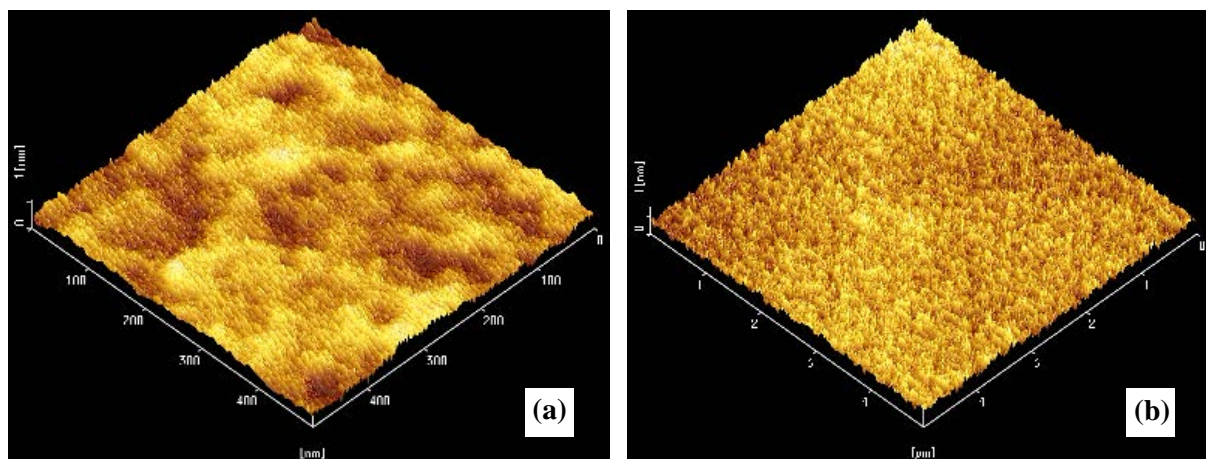


Figure 9. AFM images of the a-CN_x:H film with single-layer structure (N₂ of 70%, 500 W, 200-nm thickness). x-y axes (maximum): (a) 500 nm; (b) 5 μm, and z axes (maximum): 1 nm.

4. Conclusions

A uniform supermagnetron plasma CVD apparatus operating under a stationary magnetic field was used for a-CN_x:H film (N₂ of 0 or 70%) formation. A high deposition rate of about 85±5 nm/min was obtained at a low V_{DC}, between -20 and -62 V (rf power of between 100 and 200 W). Hard (19 ± 6 GPa) and flat (surface roughness less than 1 nm) a-CN_x:H films were successfully formed. The a-CN_x:H films with single- or double-layer structures were applied to electron field emission. The a-CN_x:H films with a double-layer structure [optical band gap: 2.2 eV (upper layer) and 1.5 eV (lower layer)] on p-Si substrate showed a low E_{TH} of 9 V/μm at 100 W for the upper layer (N₂ of 0%) and at 200 W for the lower layer (N₂ of 70%). Wide optical band gap of the upper layer is effective for reducing E_{TH} values.

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