

Field Electron-Emission from a-CN_x:H Films Formed on Al Films Using Supermagnetron Plasma CVD

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Abstract

Hydrogenated amorphous carbon nitride (a-CN_x:H) films were formed on p-Si, Al films deposited on n-Si (Al/n-Si) and glass (SiO₂) (Al/glass) substrates, using pulsed rf supermagnetron plasma chemical vapor deposition (CVD) with N₂/i-C₄H₁₀ mixed gases. The rf powers (13.56 MHz) of both the upper and lower electrodes were modulated by a 2.5-kHz pulse at a duty ratio of 12.5%. N₂ gas concentration was controlled at 70%. The optical band gap of a-CN_x:H films was about 0.75 eV. The a-CN_x:H films deposited on substrates of p-Si, Al/n-Si and Al/glass showed low threshold emission electric fields (E_{TH}) of 10, 13 and 12 V/μm, respectively. The a-CN_x:H film deposited on low-cost Al film (Al/glass) showed a sufficiently low E_{TH} of 12 V/μm, eliminating the need for high-cost p-Si substrates.

Keywords

Supermagnetron Plasma, Chemical Vapor Deposition, Amorphous Carbon Nitride, Field Emission

1. Introduction

Excellent field electron-emission characteristics of amorphous carbon films have attracted considerable attention due to their promising applicability to cold-cathode materials in future-generation high-performance electronic devices, such as display devices and microelectronics [1]-[4]. Hydrogenated amorphous carbon (a-C:H) and amorphous carbon nitride (a-CN_x:H) films are of considerable interest due to their unique properties, such as high hardness, low stress and chemical inertness [5]. Carbon nanotubes are also expected to be the future leading candidate for use as field emitters [4] [6]. However, they are deposited at relatively high temperatures of 700°C -

1000°C, which is extremely high for deposits on low-cost glass substrates [6] [7]. a-CN_x:H films can be deposited at temperatures below 400°C [8], and show excellent field-emission characteristics from their flat surfaces [2] [9]–[11]. For cold cathode operation in flat-panel displays etc., a large-area electron emission with a low working voltage is required. Detailed studies have shown that the field-emission behavior of a-CN_x:H planar structures is largely influenced by many factors 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 the preparation methods [10]–[13].

In the preparation of a-CN_x:H films by plasma chemical vapor deposition (CVD), high-speed deposition is of great use. As regards a high rate, extreme-density plasma such as supermagnetron plasma is preferable [14] [15]. The supermagnetron plasma becomes high-density at an rf phase difference of 180°, which is used for sputter-assisted and pulsed rf supermagnetron plasma CVD [16] [17]. Using this plasma, the high-rate and low-temperature deposition of a-CN_x:H layers can be achieved. The addition of N atoms to a-C:H films supports a lower electrical resistivity and a narrower optical band gap [14]. This could be caused by the increase in the sp²/sp³ ratio, the increase in the sp² cluster size or the connection of sp² clusters by N atoms [12] [18] [19]. The emission threshold field is reported to be dependent on the distribution of the sp² clusters and gives rise to the high internal field enhancement within the a-C:H films [11] [20]. Using the supermagnetron plasma, a-CN_x:H layers with low resistivity were realized. These layers have excellent field emission characteristics [17].

In this kind of study, Si substrates are frequently used for the deposition of a-CN_x:H films [9] [11] [12] [20]–[23]. To investigate differences arising from deposition substrates, we used Al films (Al deposited on n-Si and glass substrates) and p-Si wafers. As Al film is easy to prepare and inexpensive, good field electron emission from a-CN_x:H layers formed on Al film would make it practical to employ a-CN_x:H/Al structures in such products as field emission devices.

In this study, a-CN_x:H films were prepared using i-C₄H₁₀ as the hydrocarbon source and N₂ as the mixing gas. At the upper and lower electrode rf powers (UPRF/LORF) of 100 - 400/400 W, i-C₄H₁₀/N₂ mixed gas was used for the deposition of the a-CN_x:H planar structures. The physical and chemical properties of these a-CN_x:H films were controlled by adjusting the UPRF. The field emission characteristics of the a-CN_x:H films were evaluated and their dependence on the deposition substrate (Al film or p-Si substrates) was analyzed.

2. Experimental Procedures

In this experiment, a pulsed rf supermagnetron plasma CVD apparatus (**Figure 1**) was used to deposit a-CN_x:H films. Two different rf power sources with the same rf frequency (13.56 MHz) were used; their rf amplitudes were modulated using a pulse generator (P.G.: 2.5 kHz pulse of 12.5% duty ratio), and the two rf powers were supplied to the two (upper and lower) electrodes inserted into a grounded metal chamber. The upper electrode was covered with a graphite plate to prevent sputtering of the metal electrode surface. The phase difference between the two rf voltages was approximately 180° under the control of phase shifter (P.S.: 13.56 MHz oscillator with two out-puts under controlling the phase difference) to obtain the maximum deposition rate, and a rotating magnetic field (approximately 80 G) was applied parallel to the two electrode surfaces. The lower electrode (substrate holder) was heated to 100°C during film deposition. For film deposition, i-C₄H₁₀ (120 sccm) and N₂

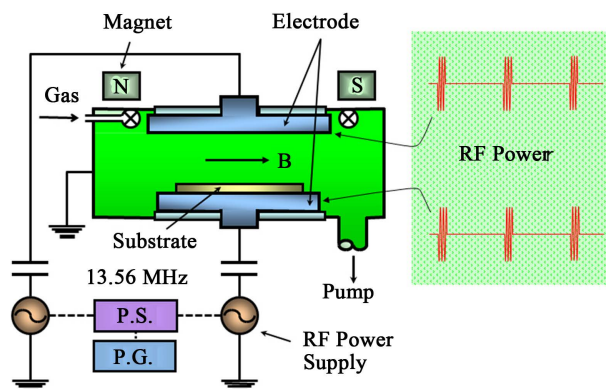


Figure 1. Schematic of the pulsed supermagnetron plasma CVD apparatus.

(50 sccm) gases were used, and the gas pressure was controlled to be 4 Pa. Profilometry (ULVAC DECTAK-3) was used to measure the film thicknesses. Using optical absorption data measured with a UV/Vis/NIR spectrometer (Shimadzu UV-3100PC), the optical band gap was estimated from a 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 [24]. 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 for FTIR analysis was controlled to be about 500 nm for all samples. The film hardness was evaluated using a dynamic ultra-micro-hardness tester (Shimadzu DUH-W201) by analyzing the displacement vs. the load curve.

3. Results and Discussion

We used a CVD apparatus of pulsed rf supermagnetron plasma under rf power modulated by a 2.5-kHz pulse frequency and a duty ratio (defined as the ratio of pulse on-time to total cycle time) of 12.5% to deposit a-CN_x:H films at the gas pressure of 4 Pa. **Figure 2** shows the UPRF (100 - 400 W) dependence of the film deposition rate on Si wafer measured at an LORF of 400 W, whose deposition rate showed slight dependence on substrate (Si or SiO₂). The deposition rate changed slightly, and was about 25 nm/min, reaching a peak (26.3 nm/min) at the UPRF of 300 W. During the off-time of the LORF, the wafer temperature became naturally lower than that of the wafer exposed to continuous discharge plasma [25] [26].

The optical band gaps of a-CN_x:H films formed on SiO₂ substrates at UPRF/LORF levels in the range 100 - 400/400 W were measured; results are shown in **Figure 3**. The optical band gap changed little, and was about 0.75 eV for all trials. From this experiment, it was found that the optical band gap depended very little on the UPRF.

The hardnesses of a-CN_x:H films formed on Si wafers at UPRF/LORF levels of 100 - 400/400 W were measured; results are shown in **Figure 4**. Hardness showed slight variation in the UPRF range of 100 - 400 W, with a value of 34 ± 2 GPa. These values were sufficiently higher than that of vitreous silica (SiO₂), which was 22 GPa, and significantly higher than those of continuous discharge plasma CVD films (below 28 GPa) [27]. This high hardness was obtained by continuous radical deposition and periodic ion bombardment over the films and a low and stable substrate temperature. The deposited C radicals would form strong sp³ bonds under periodic ion bombardment and stable temperature.

FTIR absorption spectra were measured for the a-CN_x:H films deposited on Si wafers at UPRF/LORF levels of 100 - 400/400 W, and are shown in **Figure 5**. Four kinds of absorption spectra were measured at 1100 to 1700 cm⁻¹ (C=C, C=N, and C=N-H bonds), 2190 cm⁻¹ (C≡N bond), 3030 cm⁻¹ (CH₃, CH₂, and CH bonds) and 3300 cm⁻¹ (NH bonds) [28]. Absorption spectra changed very little with the increase of UPRF from 100 W to 400 W, as with the case of optical band gap shown in **Figure 3**.

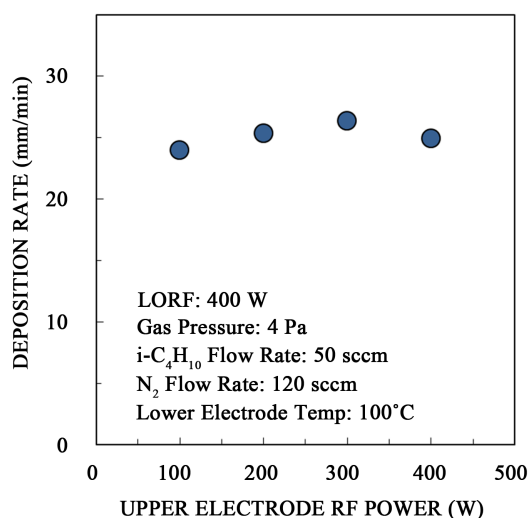


Figure 2. Deposition rate of a-CN_x:H films as a function of UPRF (100 - 400 W). LORF is 400 W.

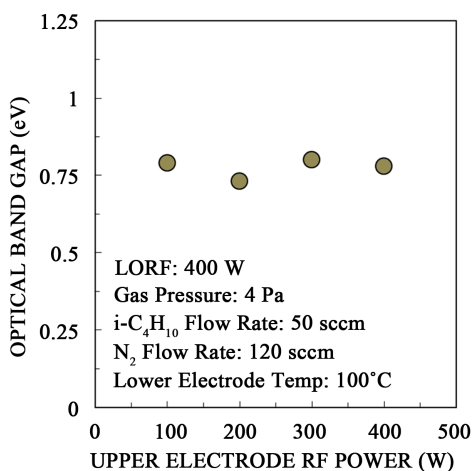


Figure 3. Optical band gap of a-CN_x:H films as a function of UPRF (100 - 400 W). LORF is 400 W.

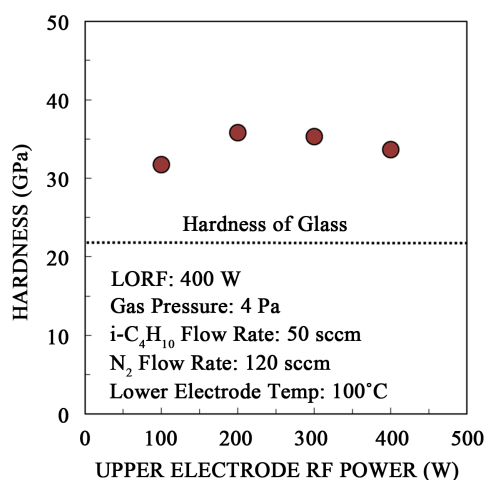


Figure 4. Hardness of a-CN_x:H films as a function of UPRF (100 - 400 W). LORF is 400 W.

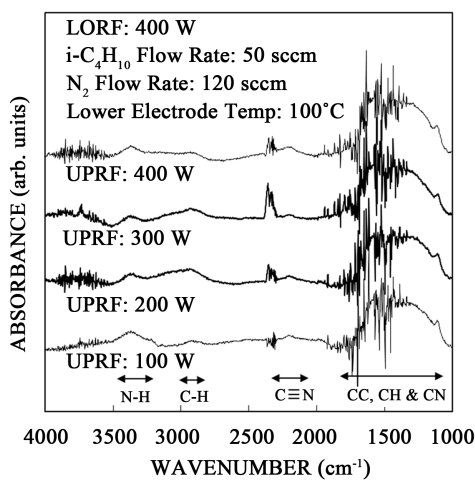


Figure 5. FTIR absorption spectra of a-CN_x:H films as a function of UPRF (100 - 400 W). LORF is 400 W.

These a-CN_x:H films of about 200-nm thickness were deposited at 200/400 W on three type of substrates: a p-Si wafer (0.02 Ωcm), 100-nm-thick Al film deposited on an n-Si wafer (0.01 Ωcm) (Al/n-Si) and 100-nm-thick Al film deposited on a glass wafer (Al/glass). Al films were deposited using Al magnetron sputter with a ring permanent magnet as previously reported by us [29]. The a-CN_x:H film deposition rates on p-Si, Al/n-Si and Al/SiO₂ substrates showed little difference. The surface morphology of p- or n-Si or glass wafer was measured using an atomic force microscope (AFM). It was observed that its surface was almost flat, and the surface roughness was less than 2 nm (p- or n-Si) or 100 nm (glass) over an area of 5 μm × 5 μm. The surface morphology of an Al/(p- or n-Si or glass) or a-CN_x:H/Al/(p- or n-Si or glass) was also measured and the surface roughness was almost flat. The surface roughness was not changed by the deposition of a-CN_x:H films, and was greatly influenced by the base substrate (p- or n-Si or glass).

The field electron emission characteristics of the a-CN_x:H films deposited on p-Si wafers are shown in **Figure 6**. The field emission sample was put on the cathode. The anode was made of a 2-mm-diameter Mo rod. The spacing between the sample surface and the anode was 50 μm. The experiment was realized in a high-vacuum system with a base pressure of about 10⁻⁵ Pa. The emission threshold electric field (E_{TH}) was as little as 10 V/μm. In this experiment, E_{TH} was defined as the applied electric field at the field emission current of 0.01 μA. The FN plot of this a-CN_x:H film, shown in the inset of **Figure 6**, was nearly linear.

The field electron emission characteristics of the a-CN_x:H films deposited on the Al/n-Si substrate put on the cathode are shown in **Figure 7**. The E_{TH} was 13 V/μm. The FN plot of this a-CN_x:H film, shown in the inset of **Figure 7**, was nearly linear. The contact between Al and n-Si is Schottky-like and that between Al and the a-CN_x:H film is ohmic.

Field electron-emission characteristics of the a-CN_x:H films deposited on the Al/glass substrate are shown in **Figure 8**. The E_{TH} was 12 V/μm. The FN plot of this a-CN_x:H film, shown in the inset of **Figure 8**, was nearly linear. In this case, Al film was connected electrically to the cathode using Al wire. This experiment shows that no Si wafers are necessary to make field emission devices.

As a reference, an Al/(p- or n-Si or glass) wafer with no a-CN_x:H films coating showed no field emissions. This indicates that a-CN_x:H film is the key material for easy field electron emission. However, the selection of the base material on which to deposit the a-CN_x:H film has a great influence on the ease of field emission. The a-CN_x:H film deposited on n-Si showed poor field emission [30]. Al film is a low-cost material compared with Si wafers. Therefore, Al film is important as the base material on which to deposit a-CN_x:H film for application to field electron-emission devices.

4. Conclusion

a-CN_x:H films were deposited using pulsed supermagnetron plasma CVD. Using rf power (upper and lower electrodes) modulated by 2.5-kHz pulse frequency, wafers were cooled and high-grade a-CN_x:H films were

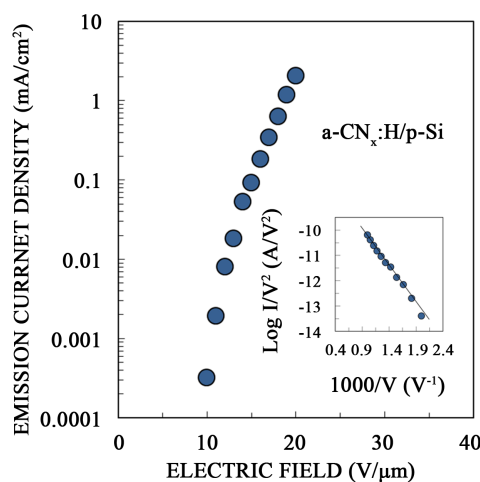


Figure 6. Emission current-voltage characteristics of a-CN_x:H film deposited on the p-Si substrate at 200/400 W. The inset shows its FN plot.

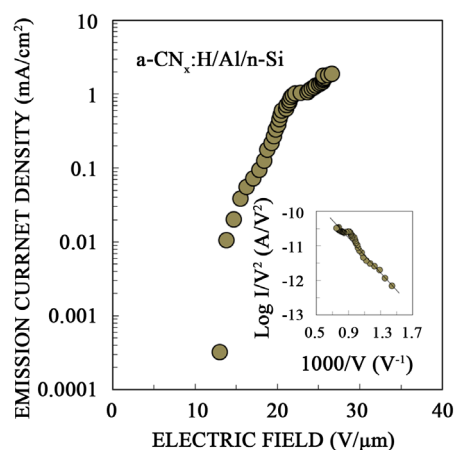


Figure 7. Emission current-voltage characteristics of a-CN_x:H film deposited on the Al/n-Si substrate at 200/400 W. The inset shows its FN plot.

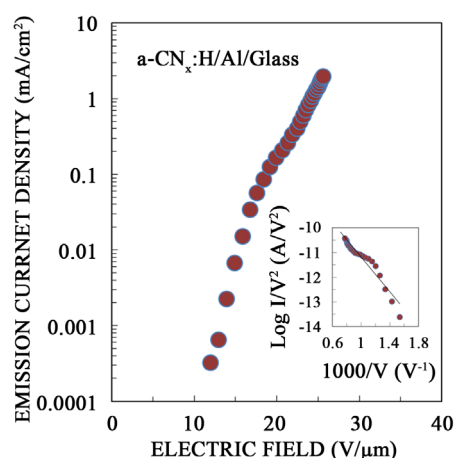


Figure 8. Emission current-voltage characteristics of a-CN_x:H film deposited on the Al/glass substrate at 200/400 W. The inset shows its FN plot.

formed. At the duty ratio of 12.5% and rf powers of 200/400 W, the optical band gap of a-CN_x:H film was 0.75 eV. The a-CN_x:H films (200/400 W) deposited on Al films formed on n-Si (Al/n-Si) and glass wafers (Al/glass) showed low E_{TH} values (high field emission ability) of 13 and 12 V/μm, respectively. From this experiment, it was found that Al film was a promising (low-cost) base material on which to deposit a-CN_x:H film for the fabrication of economical field electron emission devices.

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