23P011-O

Pulsed Supermagnetron Plasma Deposition of a-CN_x:H Films for Field Emission Use

パルス変調スーパーマグネトロンプラズマによる
電界電子放出用a-CN_x:H膜の堆積

Haruhisa Kinoshita and Tanaka Sumio
木下治久，田中純雄

Research Institute of Electronics, Shizuoka University
3-5-1 Johoku, Naka-ku, Hamamatsu 432-8011, Japan
静岡大学電子工学研究所，〒432-8011 静岡県浜松市中区城北3-5-1

Supermagnetron plasma was applied to the deposition of amorphous CN_x:H (a-CN_x:H) films. The range of electrode rf power (UPRF/LORF) was selected as 200 (Continuous)/50–800 (Pulsed) W, and films were deposited using i-C_4H_{10}/N_2 plasma. The range for the duty ratio of pulsed rf power was selected as 12.5%. The optical band gap was decreased with increases in LORF. Hardness was increased with LORF. The lowest threshold electric field was observed to be 11 V/μm at UPRF/LORF of 50-200/400 W.

1. Introduction

Amorphous carbon (a-C) films have received considerable attention due to its high chemical stability, optical transparency, high mechanical hardness with low dielectric constant. It was found that both the optical and electrical properties, as well as their mechanical properties, can be modified by nitrogen incorporation [1]. In the case of supermagnetron plasma chemical vapor deposition (CVD), it is important to control the substrate temperature from its heating by bombardment of high energy ions. Pulsed cooling using pulsed plasma is effective to avoid overheating of the substrate. Pulsed plasma CVD is effective to deposit low residual stress a-CN_x:H films [2]. Low residual stress films are effective to form electronic devices such as field emitter and photovoltaic cell with high reliability [3]. Low substrate temperature is favorable to avoid degradation of the quality of underlying layers and the reliability of electronic devices. High internal stress makes it difficult to deposit thick films by delaminating from the substrate.

2. Experiment

a-CN_x:H films were deposited using a pulsed supermagnetron plasma CVD apparatus. Two different rf power sources with the same rf frequency (13.56 MHz) were controlled to modulate rf amplitude using a pulse generator, and were supplied to two electrodes. A magnetic field of about 80 G was applied in parallel with the two electrode surfaces. The deposition substrates were placed on the lower electrode. The lower electrode was heated to 100°C during the film deposition. i-C_4H_{10} (50 sccm) and N_2 (120 sccm) were introduced into the CVD chamber, and the gas pressure was maintained at 30 mTorr. The bonding configurations of a-CN_x:H were measured by using a Fourier transform infrared (FTIR) spectrometer. The hardness of the films was determined by a dynamic ultra-micro-hardness tester. The optical band gap was estimated from the Tauc formula using optical absorption data specified by the UV/VIS/NIR spectrometer.

3. Results and Discussion

The FT-IR absorption spectra of a-CN_x films were measured, and are shown in Fig. 1. Broad absorption band of C=C, C=N, C=C, CH_2 and CH_3 bonds (1100- 1700 cm^{-1}) was observed in all the

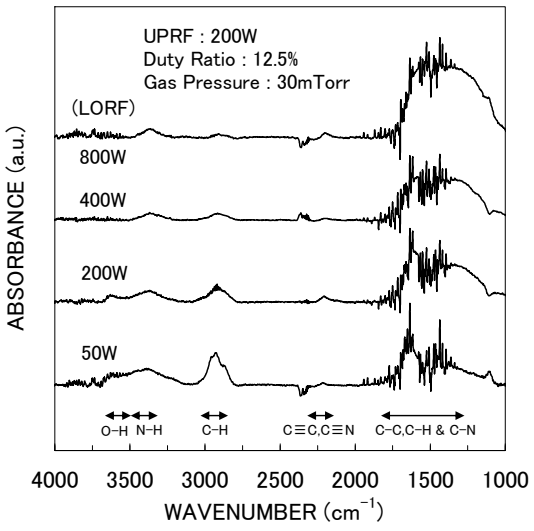

Fig. 1 Dependence of FT-IR absorption spectra on LORF.

films (LORF: 50-800 W). Absorption band at about 2930 cm^{-1} (CH_3, CH_2, and CH bonds) was decreased with the increase of LORF, however that of 3300 cm^{-1} (NH bond) was increased with the increase of LORF. That of 3500 cm^{-1} (OH bonds) was observed in two films deposited at LORF of 50 and 200 W. From these experimental data, two films deposited at 50 and 200 W were found to include many H atoms. The film deposited at 800 W included less H atoms.

Fig.2 shows the optical band gap of formed a-CN_x:H films. At LORF of 50 W, optical band gap was about 1.9 eV. It was decreased with the increase of LORF. The lowest value of about 0.6 eV was obtained at LORF of 800 W.

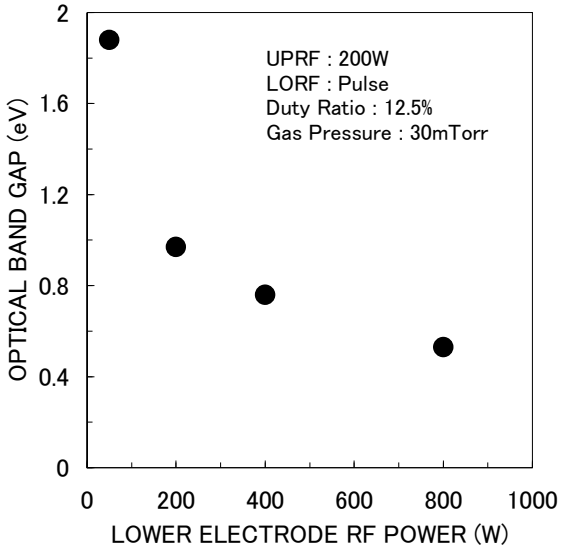

Fig. 2 Dependence of optical band gap on LORF.

The hardness was measured as a function of LORF, as shown in Fig. 3. The hardness was increased from 8 to 35 GPa with the increase of LORF from 50 to 800 W. a-CN_x film with many H atoms (LORF: 50 and 200 W) was soft and that with less H atoms (LORF: 800 W) was hard. For reference, we measured the hardness of quartz glass (SiO_2), which was 22 GPa.

These a-CN_x films of about 200 nm thickness were deposited on p-Si substrates, and their field emission characteristics were measured. The electron emission characteristics of these flat a-CN_x films were measured, as shown in Fig. 4. Emission threshold electric field (E_{TH}) was decreased from 17 to 11 V/μm with the decrease of LORF from 800 to 50 W. The films with many H atoms showed lower E_{TH} characteristics. The FN plots of these a-CN_x films shown in the inset of Fig. 4 were nearly linear.

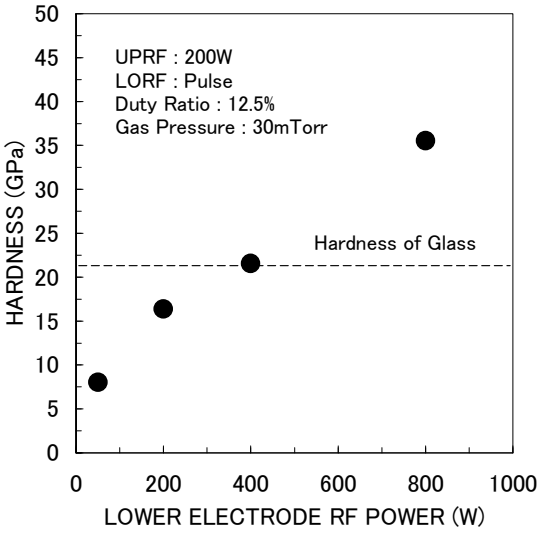

Fig. 3 Dependence of hardness on LORF.

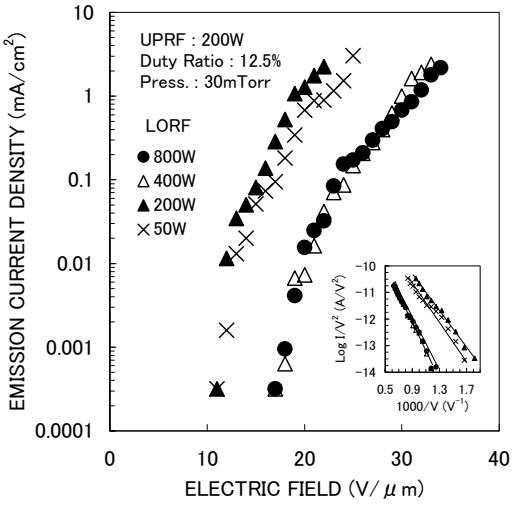

Fig. 4 Dependence of electron emission characteristics on LORF.

4. Conclusion

a-CN_x films were deposited using pulsed supermagnetron CVD. Broad absorption spectra of CH_3, CH_2, CH, NH and OH bonds were observed in the films deposited at LORF of 50 and 200 W, but not observed in that (LORF: 800 W). E_{TH} of electron field emission was decreased from 17 to 11 V/μm with the decrease of LORF from 800 to 50 W.

References

[1] P.Wood, T.Wydeven and O.Tsuji, Thin Solid Films **258**, 151 (1995).
[2] S. Kumar, P. N. Dixit. D. Sarangi and R. Bhattacharyya, J. Appl. Phys. **85**, 3866 (1999).
[3] H. Kinoshita and H. Suzuki, J. Mod. Phys., **2**, 398 (2011).