Field Emission Characteristics a-C:F:N Film Deposited by Inductively Coupled Plasma Chemical Vapor Deposition

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Abstract

Amorphous fluorocarbon (a-C:F) is of interest for low dielectric interlayer material, but in this work we applied this material to FED field emitter. N-doped a-C:F films were deposited by inductively coupled plasma chemical vapor deposition (ICPCVD). The Raman spectra were measured to study the film structure and inter-band optical absorption coefficients were measured using Perkin-Elmer UV-VIS-IR spectrophotometer and optical band gap was obtained using Tauc's plot. XPS spectrum and AFM image were investigated to study bond structure and surface morphology. Current-electric field (I-E) characteristic of the film was measured for the characterization of electron emission properties.

The optimum doping concentration was found to be $[N_2]/[CF_4] = 9\%$ in the gas phase. The turn-on field and the emission current density at $[N_2]/[CF_4] = 9\%$ were found to be 7.34 V/μm and 16 μA/cm^2 at 12.8 V/μm, respectively.

I. Introduction

Recently, Diamond-Like-Carbon (DLC) is of interest for field-emitter material due to its unique properties such as high hardness, high thermal conductivity, chemical inertness [1] and low electron affinity. However, its unstable emission current and the difficulty in patterning and processing make it difficult to apply DLC to FED emitter. On the other hand, amorphous fluorocarbon (a-C:F) is relatively soft and can be patterned and etched easily.

The a-C:F has attracted much attention recently as an interlayer dielectric material for ULSI because of its low dielectric and insulating properties[3], and in this work we applied this material to FED field emitter.

The incorporation of F atoms in amorphous carbon (a-C) was known to reduce the dangling bond density and localized states [3], and thus the electrical properties of the a-C:F can be improved compared with DLC. The substitutional doping of N in tetrahedral amorphous carbon (ta-C) and DLC films has been carried out [4-5]. The nitrogen is the best atom for n-type doping in ta-C and DLC. Nitrogen is a shallow donor compared to phosphorus, so we think that N can be a effective dopent in a-C:F. In the present work, we deposited a-C:F films by ICPCVD (Inductively coupled plasma CVD), which has a high plasma density.

II. Experiment

A mixture of CF_4 and H_2 has been used to deposit a-C:F. The RF power was applied to a planar antenna on a quartz plate and the gas mixture of $N_2/CF_4/H_2$ was introduced for deposition of N doped a-C:F. A schematic diagram of the ICPCVD is shown in Fig.1 The glass plates and silicon wafers were used as the substrates.

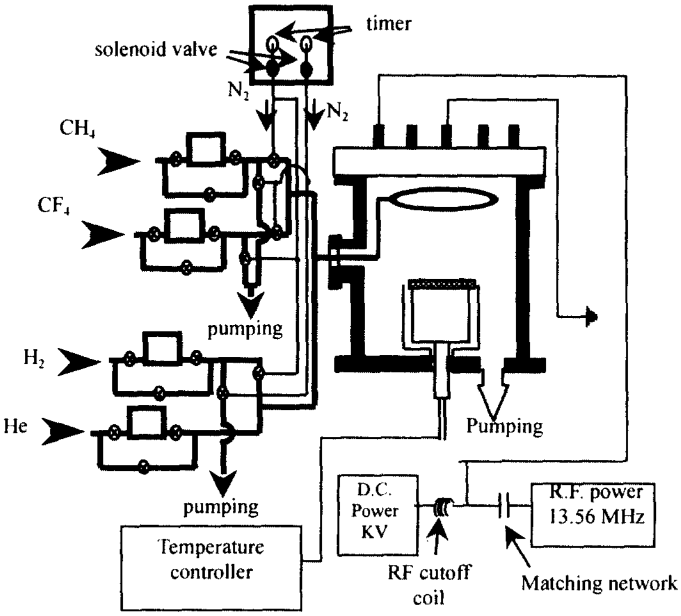


Fig. 1 A schematic diagram of the ICPCVD used in the preparation of a-C:F and a-C:F:N

During the film deposition, the substrate temperature, RF power and gas pressure were fixed at 300°C, 150 W and 20 mTorr, respectively. The flow rates of H_2 and CF_4 were varied from 1 sccm to 3 sccm and from 5 sccm to 10 sccm, respectively. The $[N_2]/[CF_4]$ flow rate ratio was changed from 0 to 20% by increasing N_2 flow rate with fixing the CF_4 flow rate 5 sccm.

The Raman spectra were measured to study film structure and inter-band optical absorption coefficients were measured by a UV-VIS spectrophotometer and optical band gap was obtained using Tauc's plot. The atomic concentrations of N and F were measured by XPS.

The electron emission behavior of N doped a-C:F films has been measured between the two parallel plates in vacuum as a function of $[N_2]/[CF_4]$ flow ratio which was utilized to deposit the films. We investigated the emission current stability of a-C:F:N.

The surface roughness of a-C:F:N films were measured before and after bias-stress by AFM to study the current induced change in the surface morphology.

III. Results

Figure 2 shows the Raman spectra of the a-C:F:N films. The Raman intensities of DLC and ta-C exhibit G (1560 cm^{-1}) and D(1335 cm^{-1}) peaks arisen by amorphous graphite and disorder of graphite, respectively. However, the G and D peaks could not be found in Fig. 2. The D and G peaks arise from carbon six fold ring and small graphite clusters and their disorder. The added F atoms break the carbon cross-link and changes the structure of the a-C. Therefore, the a-C:F:N structure appears to be different from DLC and ta-C.

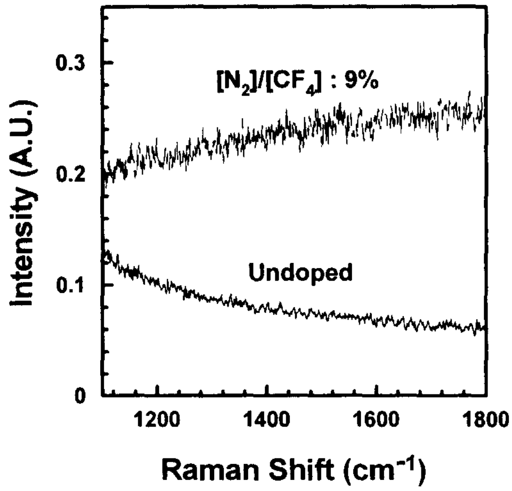


Fig. 2.The Raman spectra for the a-C:F and a-C:F:N films deposited with a gas mixture of $[N_2]/[CF_4]$=9%

The XPS spectrum of the a-C:F:N is shown in Fig. 3, showing F 1s peak at 689 eV and C 1s peak at 288 eV corresponding to the C-F, and N 1s peak at 402 eV. The spectrum shows higher peak intensity of F atoms than that of C atoms.

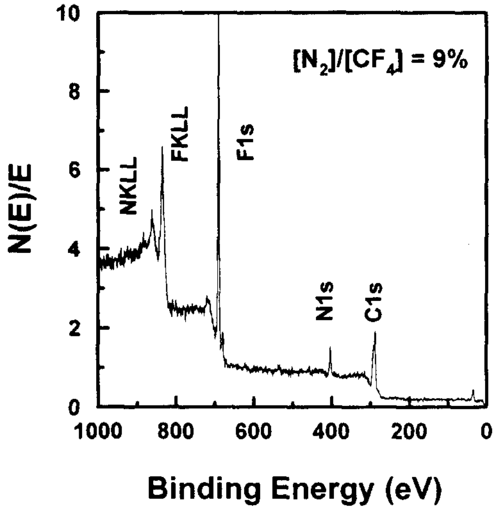


Fig. 3. The XPS spectrum of the a-C:F:N film deposited with a gas mixture of $[N_2]/[CF_4]$=9%

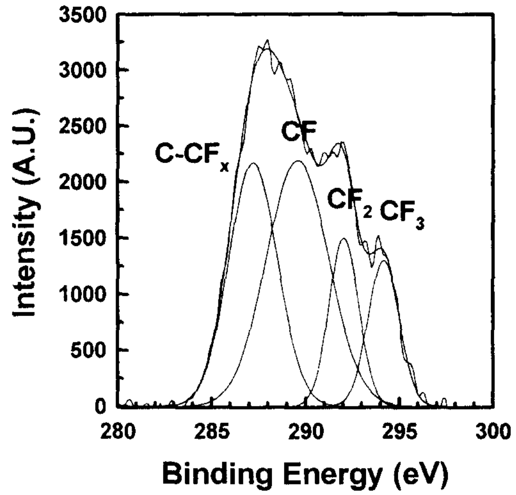


Fig. 4. The deconvolution of C1s XPS spectrum for the a-C:F:N film

Figure 4 shows the C1s XPS spectrum of the a-C:F:N deposited with a gas mixture of $[N_2]/[CF_4] = 9\%$.

The peaks were deconvoluted into four components : C-CF_x at 287 eV, CF at 289 eV, CF_2 at 292 eV and CF_3 at 294 eV. C-C or C-H_n (hydrocarbon) peak does not appear in this sample.

Figure 5 shows the current-voltage characteristics of the Al/a-C:F:N/p^+-Si devices with various nitrogen gas flow rates. The a-C:F film has high resistivity and low dielectric constant. However, in this work, it is found that the a-C:F:N films deposited with the gas mixtures between 6% and 20% show n-type conduction. The interesting properties of a-C:F:N are due to the n-type doping by N atoms in a-C:F.

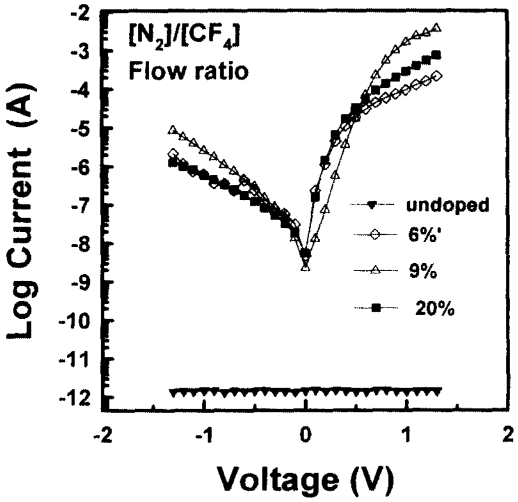


Fig. 5. The current-voltage characteristics of the Al/a-C:F:N/p^+-Si devices with different a-C:F:N film.

Figure 6 shows the current density-electric field (J-E) characteristics of the nitrogen doped a-C:F films. The electron emission current increases and turn-on field decreases with increasing $[N_2]/[CF_4]$ flow rate ratio up to 9% and then it decreases with further increasing of $[N_2]/[CF_4]$. The addition of N raises the Fermi energy level toward the conduction band edge, lowering the electron emission barrier height. However, at higher nitrogen content the material appears to change into nitrogen/fluorocarbon alloys and thus the emission barrier height increases.

Figure 7 shows the Fowler-Nordheim plots of the electron emission currents shown in Fig. 6. The slope of the straight line is related to the effective emission barrier height of the material.

The slope of the straight line decreases at first with increasing N_2/CF_4 flow rate ratio and then increases. The minimum effective emission barrier height was 0.045 eV, for the a-C:F:N film deposited with a gas mixture of $[N_2]/[CF_4] = 9\%$.

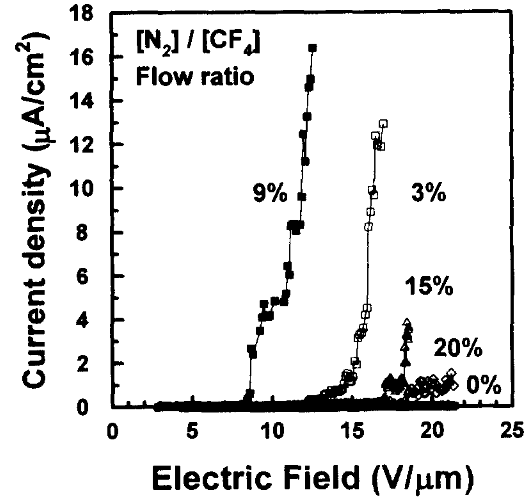


Fig. 6. Current density-electric field characteristics of the nitrogen doped a-C:F films with various [N$_2$]/[CF$_4$] gas flow rate ratios.

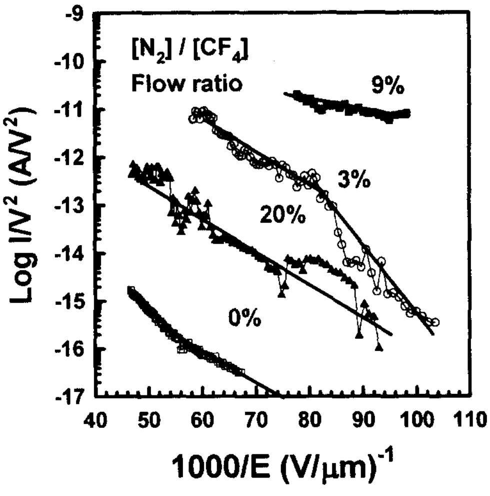


Fig. 7. The F-N plots of the emission currents for the a-C:F:N films.

Figure 8 shows the change in emission currents and current fluctuation of the nitrogen doped a-C:F films measured at a field of 15 V/μm after various bias-stress times under a field of 15 V/μm. The electron emission current and current fluctuation of the nitrogen doped a-C:F films increased at first and then stabilized with extending bias-stress time.

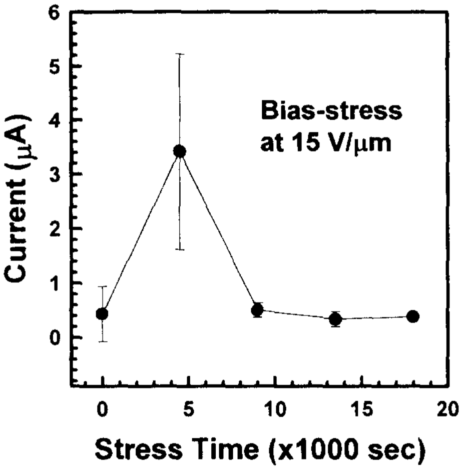
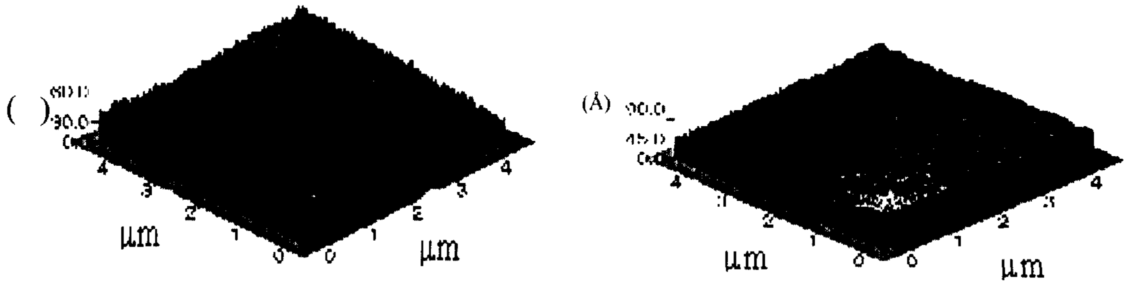


Fig. 8. The change in emission currents of the nitrogen doped a-C:F films measured at 15 V/μm after various bias-stress times under a field of 15 V/μm.



(a) (b)

Fig. 3. The AFM images of the a-C:F:N : (a) before bias-stress and (b) after bias-stress Å

Figure 9 shows the AFM images of the a-C:F:N film deposited with a gas mixture of $[N_2]/[CF_4]$ = 9% before(a) and after(b) the bias-stress for at a field of 15 V/µm. The rms roughness decrease from 8.5 Å to 4.5 Å after the bias-stress. The roughness of an initial surface is similar to that of typical DLC, but the surface appears to be modified during bias-stress. We could not find any surface damage induced by field emission experiments.

IV. Conclusion

We have developed new FEA material a-C:F:N deposited by ICPCVD with a gas mixture of CF_4 and N_2. The structure of the deposited films were found to be different from DLC and ta-C, and the a-C:F exhibited a high electron emitting behavior. The a-C:F:N can be patterned and etched and thus this material appears to be suitable for FED emitter. The optimum doping concentration was found to be $[N_2]/[CF_4]$ = 9% in the gas phase. The turn-on field and the emission current density at $[N_2]/[CF_4]$ = 9% were found to be 7.34 V/ m and 16 A/cm^2 at 12.8 V/ m, respectively.

Acknowledgment

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