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Effects of Sulfur Concentration on the Electron Field Emission Properties of Nanocrystalline Carbon Thin Films

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ABSTRACT

The electron field emission properties of sulfur-assisted nanocrystalline carbon (n-C: S) thin films grown on molybdenum substrates by hot-filament CVD technique using methane-hydrogen (CH_4/H_2) and hydrogen sulfide-hydrogen (H_2S/H_2) gas mixtures were investigated. The field emission properties of the S-assisted films are reported as a function of sulfur concentration. The incorporation of S caused structural and microstructural changes that were characterized with SEM, AFM and Raman spectroscopy (RS). The S-assisted films show smoother surfaces and smaller grains than those grown without. The lowest turn-on field measured was around 4.5 - 5.0 V/μm films grown with 500 ppm of hydrogen sulfide and at 900 °C. The electron field emission properties of S-assisted films were also compared to those grown without sulfur (i.e., intrinsic). An inverse correlation between the threshold field (E_c) and sulfur concentration was found. These finding are attributed to defect induced states within the electronic band structure.

INTRODUCTION

Cold cathodes as electron field emitters are potentially useful for field emission displays (FEDs) [1-3]. Recently, electron field emission (EFE) from diamond, disordered carbon and diamond-like carbon (DLC) attracted a great deal of interest for applications that require thin film cathodes and low threshold fields, in contrast to sharp metal tips (Spindt), such as flat panel displays (FPDs) [4-6]. In addition, DLC FED's are expected to be more cost-effective than the Spindt tips due to their complicated fabrication process [1]. Moreover, the excellent mechanical and chemical stability of carbon-based materials will result in highly reliable and stable emitters, even under extreme conditions.

In spite of the fact that the original work on electron field emission from diamond was motivated by the discovery of its negative electron affinity (NEA) [7], the ease of emission from many carbon materials suggests that the NEA is not a prerequisite. So far, there is lack of agreement regarding the mechanism(s) for FE, and more general emission models are desirable [8].

Although, much research has been devoted to the emission from disordered [5] and nanostructured carbon [9], a detailed investigation of the influence of impurity incorporating elements concentration is of interest for application issues as well as for fundamental understanding. The field emission properties for the undoped and doped (N, P, B) materials have been studied by several authors [9-14]. In this study, we report our findings of the EFE properties on n-C: S thin films grown by HFCVD as a function of sulfur concentration, keeping

the substrate temperature fixed at 900 °C, and the corresponding microstructural characterization. These results are also compared with those grown without sulfur (i.e., intrinsic). Recent pioneer reports on the addition of sulfur in diamond as a donor dopant, both experimental and theoretical modeling [14-17], stirred great interest in the diamond community. The n-type dopants of diamond (like N, P and now S) have the potential to enhance the electron field emission properties of disordered and nanocrystalline carbon films by providing electrons close to the conduction band. Studies of the changes in the electron field emission properties upon sulfur addition have not been conducted so far, except for the substrate temperature dependence keeping the sulfur concentration fixed [18].

EXPERIMENTAL DETAILS

The nanocrystalline carbon thin films in this study were prepared in a custom-built hot filament chemical vapor deposition (HFCVD) reactor, described elsewhere in detail [18]. The films were grown on mirror-polished molybdenum (Mo) disks of 1.4 cm diameter. All of the substrates were ultrasonically cleaned thoroughly in methanol for 15 min. They were then dried in He and placed immediately on a molybdenum substrate holder that is integrated with a graphite heater. The chamber was evacuated to 10^{-7} Torr or less before admitting the clean reactive gas mixture (s).

During the growth process for the intrinsic material a 2% CH_4:H_2 gas mixture with a total flow of 100 sccm was directed through a heated Rhenium (Re) filament. Eight cm of Re wire of 0.5 mm diameter was coiled, positioned 8 mm from the substrate, and Joule heated to 2400-2500 °C as measured by an optical pyrometer (Dual-wavelength, Mikron M90 Model). The Mo substrate was mounted on a graphite heater to intercept the excited gas downstream from the filament. It was maintained at 900¯930 °C during the growth process and the total gas pressure was kept at 20 Torr. Real-time SE was used to calibrate the true temperature of the substrate surface. A polished commercial Si substrate was used for the calibration, and the E_1 transition energy from a line-shape analysis of the second derivative of the dielectric function provided the temperature of the surface, through the relationship $T[K] = \{3.486-E_1 (eV)\}/4.07x10^{-4}$ [18]. The resulting true temperature of the surface is typically ~ 30 °C higher than that if measured directly by thermocouple embedded in the heater block. Besides the above mentioned conditions, in order to incorporate sulfur (S) in the samples, hydrogen sulfide (H_2S): hydrogen (H_2) premix gas mixture was introduced in the chamber along with CH_4:H_2 mixture as feedstock gas. The S-assisted films were grown at various sulfur concentration ranging 500 ppm to 100 ppm with an interval of 100 ppm at a fixed substrate temperature of 900 °C. Some amount of sulfur becomes incorporated and hence the n-C: S notation. This presumption was corroborated and quantified by the surface analytical techniques such as energy dispersive x-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS).

Typical film thicknesses were around 0.5 μm for all of the samples, measured mechanically using Tencor surface profilometer (Alpha Step 100). The surface morphology was investigated using scanning electron microscope (JEOL Model 35 CF) and atomic force microscopy (Nanoscope IIIa, Digital Instruments Inc.). Raman spectroscopy is used to analyze the structural phases in the films. The Raman spectra were recorded using a triple monochromator (ISA Jobin-Yvon Inc. Model T64000) with around 1 cm^{-1} resolution using

514.5 nm line of Ar^+- laser. The spectra were recorded using 80x objective, and the probed area was about 1-2 μm^2.

A field emission (FE) system consists of a metal base making electrical contact to the Mo substrate and a Mo anode (area = 0.071 cm^2) attached to a micropositioner for varying the cathode-anode (d_{C-A}) spacing with an accuracy of ± 5 μm. A Keithley 6517 electrometer with a detection limit of 10-20 pA was used for measuring the emitted current and a Bertran 210-05R high voltage power supply. Measurements of the I-V characteristics were performed in a high vacuum of 10^{-7}-10^{-8} Torr. The turn-on voltage was defined as the voltage required to produce a current of 1 nA and the electric field was computed as E_c = applied macroscopic voltage/ cathode-anode spacing (V/d_{C-A} [19, 20].

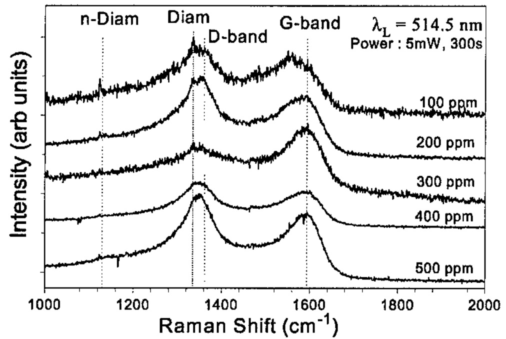

Figure 1. Raman spectra for S- assisted nanocrystalline carbon thin films as a function of sulfur concentration ([S]) depicting the characteristic diamond, graphitic and disordered carbon signatures.

RESULTS AND DISCUSSION

The Raman spectra for the S-assisted nanocrytalline carbon (n-C: S) thin films grown by HFCVD as a function of sulfur concentration is shown in Figure 1. All of the samples were grown at a substrate temperature of 900 °C. The film grown with 100 ppm shows the dominant 1332 cm^{-1} (fingerprint of diamond or sp^3 bonded C). Qualitative inspection of Figure 1 also shows broad features at 1150, 1340 and 1580 cm^{-1} typical of nanocrystalline diamond (n-D) and disordered carbon dominated by microcrystalline graphitic inclusions, [20, 21] denoted by D- and G- band respectively. These latter features predominate with respect to the increase in sulfur concentration. While the film grown with 100 ppm is quite similar to intrinsic material (n-C), one

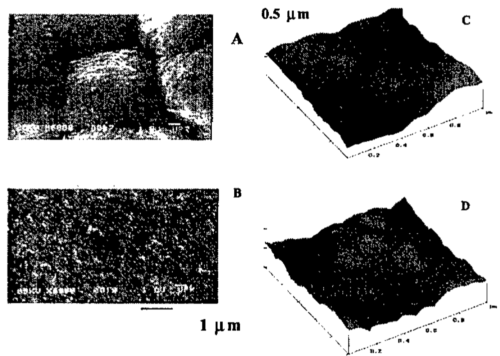

Figure 2. Typical scanning electron (A and B) and the corresponding atomic force micrographs (C and D) of nanocrystalline carbon thin films grown by S-assisted HFCVD exhibiting the change in surface morphology on sulfur addition: (A and C) 2.0% CH_4, no sulfur is incorporated in chamber, (B and D) 2.0 % CH_4, 500 ppm H_2S. All of these samples are grown at substrate temperature of 900 °C.

can note the disappearance of diamond peak right at 300 ppm of hydrogen sulfide concentration. The relative heights of the Raman peaks (D- and G-bands) differ in general. The difference among the Raman spectra can be explained by the sulfur additions. Under the specific growth condition considered in this study, sulfur tends to introduce disorder and defects considerably, similar to nitrogen incorporation, which induces graphitization of carbon films [22-24]. Changes in the surface morphological features are apparent from SEM and AFM techniques (see Figure 2). The ball-like morphology transforms to fine-grained on S-addition and the surface becomes relatively smoother. The grain size estimated using AFM increased from 20 to 60 nm upon decreasing the sulfur concentration. In addition, the grain size distributions range from 20-60 nm to 100-150 nm. The rms surface roughness estimated from AFM becomes reduced from 64 nm (for intrinsic) to 25 nm (for S-assisted). For a particular hydrogen sulfide concentration of 500 ppm and a growth temperature of 900 °C, the amount of sulfur introduced to the films was quantified to be around 0.5 % - 1.0 % from EDX and XPS surface analytical techniques.

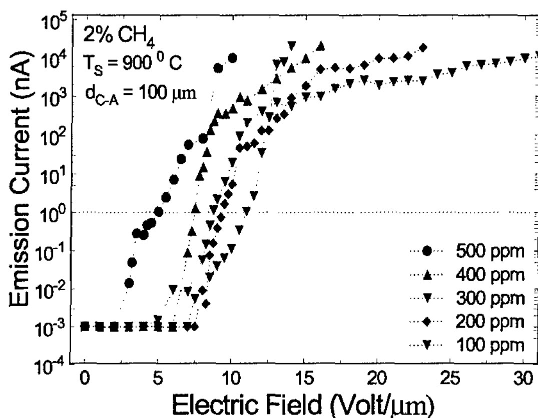

Figure 3. Electron filed emission I-V curves for the S-assisted nanocrystalline carbon thin films as a function of sulfur concentration ([S]) deposited by hot-filament CVD. The dotted line (---) is the reference current (1 nA) to define the turn-on field (E_c).

Figure 3 shows the typical I-V characteristics obtained experimentally for these n-C: S films as a function of sulfur concentration. The measurements were not taken above 20-25 μA in order to prevent 'breakdown'. The lowest turn-on field achieved is ~ 4.5 – 5.0 V/ μm for the sample grown with 500 ppm H_2S, while for the 100 ppm it is 10.5 -11.5 V/μm, which is around the same as for the intrinsic material (n-C). On qualitative comparison with the previous studies using nitrogen and oxygen, the films grown with higher nitrogen to oxygen ratio have shown a great promise in terms of EFE characteristics, in contrast to lower ratios and even oxygen alone [21-25]. Therefore, the

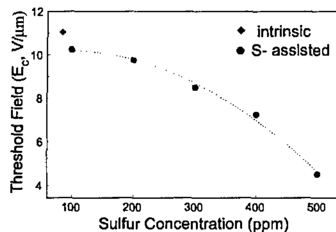

Figure 4. Shown is the variation of E_c and sulfur concentration. The dotted line is shown to guide the eye.

results obtained hereby are closer to nitrogen-like than oxygen-like [20]. The reason(s) for this behavior or characteristics is not apparent and is therefore a subject of speculation. Because of sulfur addition to the CVD process, there is a substantial amount of structural defects that become introduced distorting the lattice. These defects create additional energy bands within the bandgap of diamond and thus contribute electrons for emission at low electric fields. As initially addressed by Zhu *et al.* [26], the more the defective the diamond and diamond-like material, the better the emitter it is. Combining these results with the influence of sulfur concentration, two interesting noteworthy features can be seen from Figure 3: (i) the impact of sulfur concentration on the threshold field (E_c); the higher the sulfur concentration, the lower the E_c, and (ii) the exponential increase of the current amplitude at the highest sulfur concentration. This may be attributed to the tailing of the valence band maxima and conduction band minima, upon the introduction of midgap states. This scenario is more probable at higher sulfur concentration than at the lower ones. The reduction in E_c with sulfur concentration is plotted in Figure 4, which provides an inverse correlation between E_c and sulfur concentration within the range of our study. Similar observations have also been found for nitrogen-doped amorphous carbon materials [20-24] and metal-oxide-semiconductor (MOS) structures by several authors [27-29].

CONCLUSIONS

The field emission properties for the S-assisted films were investigated as a function of sulfur concentration. Low-field electron emission values were observed at 4.5-5.0 V/μm for films grown at the highest sulfur concentration (500 ppm H_2S). On comparing these results with the intrinsic material, the E_c is found to be almost half, thus indicating a strong effect of sulfur addition. The S-assisted films are relatively fine-grained and smoother. Under the specific growth condition considered in this study, sulfur tends to introduce disorder and defects considerably, similar to nitrogen incorporation. Thus sulfur incorporation in carbon films behaves similar to nitrogen doping in disorder or amorphous carbon thin films. An inverse correlation between E_c and sulfur concentration was found. The addition of sulfur enhances the field emission properties of n-C rendering it a viable cold cathode material.

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REFERENCES

1. C. A. Spindt, I. Brodie, L. Humphrey and E. R. Westerberg, J. Appl. Phys. **47**, 5248 (1976).
2. J. A. Castellano, in *Handbook of Display Technology* (Academic Press, New York, 1992).
3. J. E. Jaskie, Mater. Res. Bull. **21**, 59 (1996).
4. J. Robertson, Mater. Res. Soc. Symp. Proc. **509**, 83 (1998) and references therein.
5. A. Hart, B. S. Satyanarayana, W. I. Milne and J. Robertson, Diamond and Related Materials **8**, 809 (1999).

6. A. V. Karabutov, V. I. Konov, S. M. Pimenov, E. D. Obraztsova, V. D. Frolov, V. G. Pereverzev and A. A. Smolin, J. Wide Bandgap Materials **7**, 68 (1999).
7. F. J. Himpsel, J. A. Knapp, J. A. Van Vechten and D. E. Eastman, Phys. Rev. B **20**, 624-627 (1979); J. Van der Weide and R. J. Nemanich, Appl. Phys. Lett. **62**, 1878 (1993).
8. J. Y. Shin, H. K. Baik and K. M. Song, J. Appl. Phys. **87**, 7508 (2000).
9. G. A. J. Amartunga, S. R. P. Silva, Appl. Phys. Lett.**68**, 2529 (1996); M. W. Geis, N.N. Efremow, J.D. Woodhouse, and M.D. McAleese, IEEE Trans. ED Lett. **12**, 456 (1991).
10. K. Okano, S. Koizumi, S. R. P. Silva, and G. A. J. Amartunga, Nature, **381**, 140 (1996).
11. C. Wang, A. Garcia, D. C. Ingran, M. Lake and M. E. Kordesch, Electronics Lett. **27**,1459 (1991).
12. A. A. Tallin, L. S. Pan, K. F. McCarty, T. E. Felter, H. J. Doerr, R. F. Bunshah, Appl. Phys. Lett. **69**,3842 (1996).
13. B. F. Coll, J. E. Jaskie, J. L. Markahm, E. P. Menu, A. A. Talin, P. VonAllmen, Mater. Res. Soc. Symp. Proc. **498**, xx (1998).
14. J. Shiao, C. A. Zorman and R. W. Hoffman, Mater. Res. Soc. Symp. Proc. **349**, 465 (1994).
15. R. Kalish, A. Reznik, C. Uzan-Saguy and C. Cytermann, Appl. Phys. Lett. **76**, 757 (2000) and references therein.
16. D. S. Dandy, Thin Solid Films **381**, 1 (2001).
17. M. N. Gamo, C. Xiao, Y. Zhang, E. Yasu, Y. Kikucji, I. Sakaguchi, T. Suzuki, Y. Sato and T. Ando, Thin Solid Films **382**, 113 (2001).
18. S. Gupta, B. R. Weiner and G. Morell, Diamond and Related Materials 2001 (in Press); S. Gupta, B. L. Weiss, B. R. Weiner and G. Morell, Mater. Res. Soc. Symp. Proc. xx (2001) (to be published).
19. O. Groning, O. M. Kuttel, P. Groning, and L. Schlapbach, J. Vac. Sci. Technol. B **17**, 1970 (1999) and references therein.
20. B. L. Weiss, A. Badzian, L. Pilione, T. Badzian and W. Drawl, J. Vac. Sci. Technol. B **16**, 681 (1998).
21. R. J. Nemanich, J. T. Glass, G. Luckovsky, and R. E. Sroder, J. Vac. Sci. Technol. A **6**, 1783 (1988).
22. A. C. Ferrari and J. Robertson, Phys. Rev. B **61**, 14 095 (2000).
23. S. Bhattacharyya, K. Walzer, H. Hietschold and F. Richter, J. Appl. Phys. **89**, 1619 (2001).
24. J. Shiao, C. A. Zorman and R. W. Hoffman, Mater. Res. Soc. Symp. Proc. **349**, 465 (1994).
25. R. Haubner, S. Bohr and B. Lux, Diamond and Related Materials **8**, 171 (2000).
26. I. H. Shin and T. D. Lee, J. Vac. Sci. Technol. B **18**, 1027 (2000).
27. W. Zhu, G. P. Kochanski and S. Jin, Mater. Res. Soc. Symp. Proc. **509**, 53-58 (1998); W. Zhu, G. P. Kochanski, S. Jin and L. Seibles, J. Vac. Sci. Technol. B **14**, 2011 (1996).
28. N. S. Xu, J. Chen and S. Z. Deng, Appl. Phys. Lett. **76**, 2463 (2000).
29. G. Pananakis, G. Ghibando, R. Kies and C. Papadas, J. Appl. Phys. **78**, 2635 (1995).