Tailoring the electronic properties of CVD nanocrystalline diamond films by *in situ* nitrogen incorporation for selective electrochemical detection of neurotransmitters

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CVD nanocrystalline diamond films are promising materials for field emission devices, microelectrodes, and NEMS applications due to the material properties such as chemically inert, mechanically hard, and biocompatible. We have reported on nanodiamond film for field emission devices [1] and chemical sensing [2]. In this work, we tailor the electronic properties of nanodiamond films by *in situ* nitrogen incorporation for selective electrochemical sensing of neurotransmitters.

Different nitrogen contents of nanodiamond films were grown in a microwave plasma enhanced CVD machine using $H_2/CH_4/N_2$ gases, keeping the H_2/CH_4 ratio (9:1) constant and increasing the N_2 flow rate for 15sccm, 30sccm, 60sccm and 90sccm labeled as film S0, S1, S2, and S3. SEM study shows complete and conformal nanodiamond coverage for all films with surface morphology changes from a distinct 'ridge'-like to a more 'cauliflower'-like nano-structures as the N_2 flow rates increased. XPS C1s spectra indicated presence of carbon-nitrogen bonding in addition to the sp^3 and sp^2 hybridized carbon-carbon bonds. The peaks fit at 284.6eV and 285.4eV, contributed by sp^2 C-C and sp^3 C-C hybrized bonds. The sp^3 peak intensity decreases (while the sp^2 increases) with increased N_2 flow rate. The peaks locate at 286.5eV and 287.5eV correspond to C-N and C_3N_4, respectively, and both of these peaks consistently increase in intensity with increased N_2 flow rate.

Cyclic voltammograms were used for characterizing the electrochemical and bio-sensing properties. The background scan at 100mV/s in 0.1M PBS at physiologic pH 7.4 revealed a working potential window of ~3.0 V for all the films. However, films S0 and S1 show distinctly different and better sensitivity for detection of dopamine as compared to S2 and S3. Films S0 and S1 showed very well defined redox peaks detectable due to dopamine/o-quinone redox reactions. Films S2 and S3 were also able to detect presence of dopamine but with poor peak definition and wide peak-peak separation, exhibiting sluggish reaction kinetics and the peak definition was completely lost at 1mM DA and at scan rates greater than 50mV/s. The findings demonstrate that a controlled amount of nitrogen incorporation in naodiamond film (S0 and S1) is vital to maintain superior bio-sensing behavior, however, higher N_2 inclusion (S2 and S3) degrades the sensing response due to change in surface morphology and increase in CN and C_3N_4 bonds.

In this work, we have successfully tailored the electronic properties of CVD nanodiamond films for selective detection of dopamine, serotonin, epinephrine, and acetylcholine independently, as well as in the presence of ascorbic acid and uric acid, without any surface modification, hence real-time detection with long-term stability and reliability.

[1] K. Subramanian, W.P. Kang, J.L. Davidson, *IEEE Electron Device Letters* **29**, 1259 (2008).

[2] S. Raina, W.P. Kang, J.L. Davidson, *Diam. and Rel. Mat.* **17**, 896 (2008).