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Development of Diamond-Like Carbon Deposition Processes and Microfabrication of Thin-Film Ag/AgCl Reference Electrodes

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Abstract:

The ability to track neurotransmitters at a cellular level could greatly expand our understanding of the brain. To do this, however, we need to make safe, implantable devices that can sense activity at this level. This summer, two aspects of this project were focused on: a) the use of diamond-like carbon as a biocompatible coating for these devices, and b) the fabrication of thin-film silver/silver chloride (Ag/AgCl) electrodes to measure concentration of neurotransmitters. Due to its favorable properties, diamond-like carbon could reduce glial scarring and improve durability of these sensors. It was deposited using different gas mixtures by an rf-plasma enhanced chemical vapor deposition (PECVD) system. Unfortunately, only amorphous carbon was formed during this process. However, annealing at 600°C for 30 minutes in a sealed ampoule left traces of diamond-like carbon. Next, microfabrication of a Ag/AgCl thin-film electrode was completed. This electrode can be used as a reference for cyclic voltammetry to measure concentration of neurotransmitters in the brain.

Introduction:

Diamond-like carbon (DLC) has many advantageous properties, such as high wear resistance, hardness, biocompatibility, and a low coefficient of friction, that allow it to be such a promising material for biomedical applications. Radio frequency plasma enhanced chemical vapor deposition (rf-PECVD) using methane (CH_4) as a carbon precursor is one way to deposit DLC [1]. Diluting CH_4 with an inert gas, such as N_2, He, or Ar, is believed to assist the creation of capacitive coupled plasma and to enhance the plasma density [2].

Cyclic voltammetry is the process by which voltage is swept between two values at a fixed rate, and current is measured and plotted. This plot is called a voltammogram. Voltammograms can be used to quantify neurotransmitter types and concentration. To run cyclic voltammetry, however, a stable reference electrode, such as a silver / silver chloride (Ag/AgCl) electrode, is needed. It is also necessary to microfabricate this electrode to allow for a maximum amount of these devices to be put in the brain sensing system.

Experimental Procedure:

DLC films were deposited onto bare silicon wafer pieces by different ratios of CH_4 and either N_2, He, or Ar gas mixtures. Before deposition, there was a 5-minute chamber clean with 100 sccm of N_2 at 300 watts. During deposition, the rf-power was 150 W, and the deposition time was kept constant at ten minutes. The deposition pressure was kept at 300 mTorr. There was a constant total gas flow of 100 sccm for all trials and a substrate temperature of 20°C. Films were then characterized using Raman spectroscopy. The spectra showed that there was a very high concentration of hydrogen in the films, so DLC was not formed. Thus, one sample was annealed with N_2 gas at 600°C in a mini-brute furnace for 30 minutes. It was necessary to seal this sample in a glass ampoule to prevent oxidation of the film.

The Ag/AgCl electrode that was fabricated was made of multiple layers. First, layers of silicon dioxide (SiO_2, conductive layer), titanium and palladium (adhesive layer), and Ag were deposited. After this, the Ag layer was chlorinated. This was carried out through electrochemical chlorination in an HCl solution at a constant current of 1000 $\mu A/cm^2$ for 10 minutes [3].

Results and Conclusions:

The deposition rates of the DLC films, depending on the ratio of N_2/CH_4 and He/CH_4, are shown in Figure 1. The figure shows that deposition rate increased up to about 70% N_2 or He, and then decreased. This observation is similar to that observed by Kim, et al. [2], with a gas mixture of Ar/CH_4. This drop most likely occurred because when the CH_4 concentration got too low, the etching rate—due to the diluting gas—became greater than the deposition rate of CH_4.

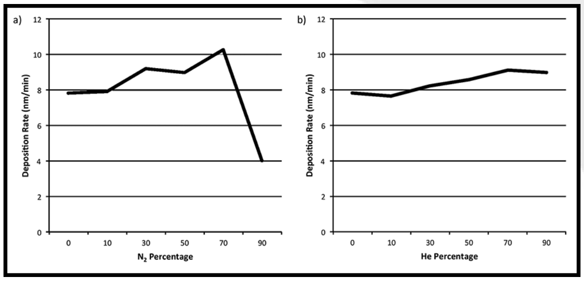

Figure 1: Variation of DLC deposition rates of the; a) N_2/CH_4 and b) He/CH_4 gas mixtures.

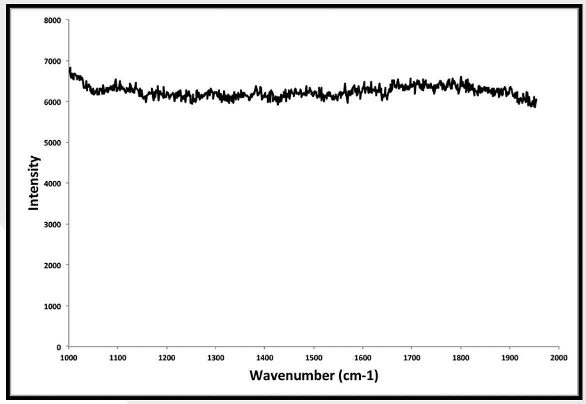

Figure 2: Raman spectra for 50% CH_4 / 50% N_2 sample.

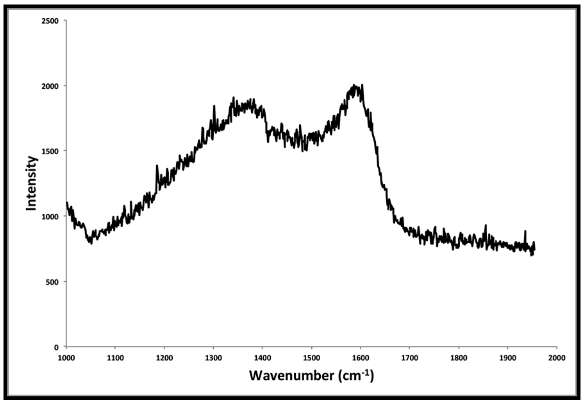

Figure 3: Raman spectra for annealed sample.

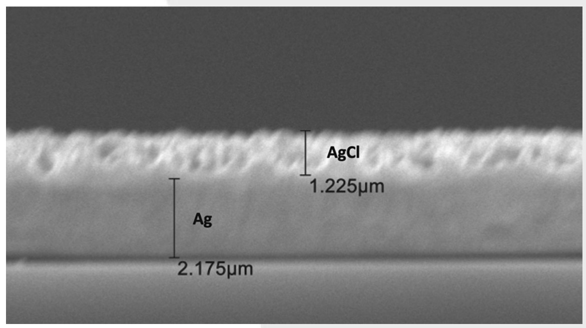

Figure 4: SEM cross-section of Ti/Pd/Ag/AgCl electrode.

After characterizing the films using Raman spectroscopy, it was shown that DLC had not formed. As shown in Figure 2, the G-peak (1600 cm^{-1}) and D-peak (1350 cm^{-1}) that are representative of sp^2 and sp^3 hybridized carbon, respectively, were not present in the spectra. We believe that this was due to the high concentration of hydrogen in the films. After annealing, however, the hydrogen was removed from the film and sp^2 and sp^3 C-C bonds were formed. Figure 3 shows the spectra for this annealed sample, and both the G-peak and D-peak are present.

After this process was done, the thin-film Ti/Pd/Ag/AgCl electrode was microfabricated. Figure 4 shows a scanning electron microscope (SEM) cross-section image of the final film. It shows about 1.2 μm of AgCl and 2.2 μm of Ag. Therefore, about 36% of the original Ag film was converted to AgCl. This agrees with the work of Huang, et. al., ran the same process and had 33.3% of the Ag film converted to AgCl [3].

Future Work:

Once DLC films are made, stress tests and biocompatibility tests will be done to gain further information on the material.

Next steps in work with the Ag/AgCl electrode include patterning the electrode and running cyclic voltammetry tests with different neurotransmitters.

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References:

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