Optimization of Diamond-Like Carbon Coatings for Medical Applications

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Surgical procedures require instruments that can withstand aggressive environments within the human body and during the sterilization processes. Due to its high corrosion and wear resistance as well as antibacterial properties, diamond-like carbon (DLC) has become the material of choice for protective coatings in the biomedical sector. DLC with high sp^3 content can be produced by plasma assisted chemical vapor deposition (PACVD); however, synthesis conditions must be optimized to yield DLC films with the desired properties.

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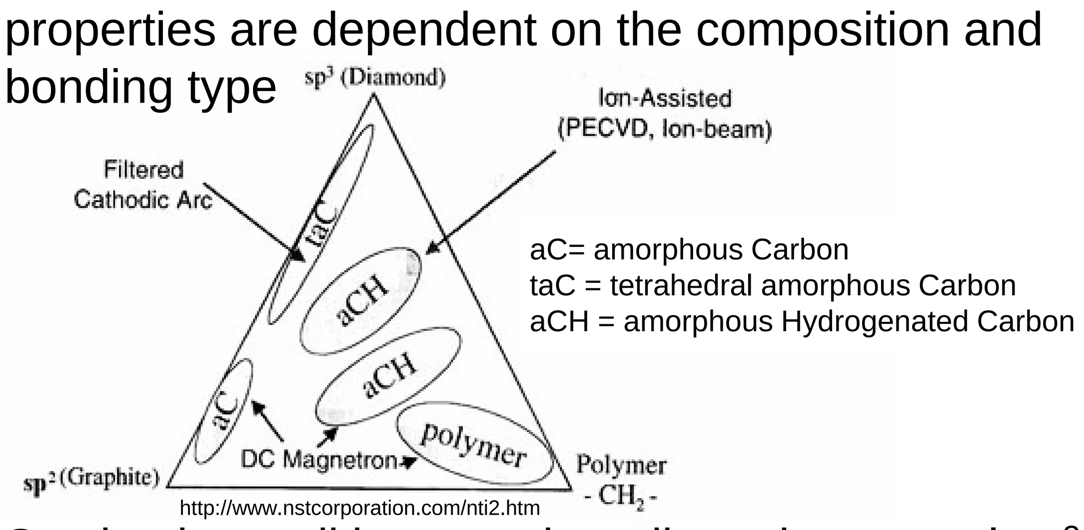
Background

- DLC is a type of amorphous carbon where properties are dependent on the composition and bonding type



- Synthesis conditions can be adjusted to control sp^3 content, during PACVD
- DLC coatings are considered "acceptable" if sp^3 carbon exceeds 30%, resistivity reaches >1GΩ without dielectric breakdown, and contains a microhardness >5 GPa [1]

Objective

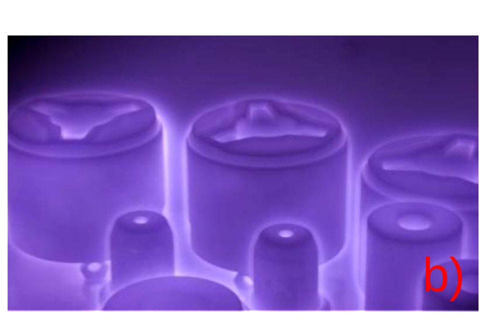
The project is aimed to optimize PACVD process in order to obtain high quality DLC coatings.

Experimental Procedure

Material Synthesis

PACVD (Rübig PN 70/90)

- Plasma decomposes precursor gases, and reactants form a solid state coating on substrate.



a) PACVD Instrument
b) Plasma glow around product in situ coating

Material Characterization

Raman Spectroscopy (Thermo Scientific DXR Raman Microscope)
-for sp^3 content

- Raman probes sp^2 and sp^3 molecular vibrations that can be used to estimate composition
- Raman data calibrated with an Si wafer, and collected at 50x magnification, using a 532 nm laser wavelength

Scanning Electron Microscopy, SEM (Phenom Desktop)
-for microstructure

- Cross sectional views estimate coating thickness while surface images provide qualitative insight to coating porosity and density
- Micrographs taken at 5,000x magnification, with 15 kV accelerating voltage

Indentation Testing (Hysitron Ti 950 Triboindenter)
-for microhardness

- All indents made with Berkovich tip and 5 second incremental load-hold-unload cycle

High Potential Testing, HiPot (Megger MIT 330)
-for resistivity

- High potential (HiPot) tests conducted with an applied voltage of 1 kV
- Sample passes test as nonconductive, if the measured current is greater than 1 GΩ, and consistent along the sample

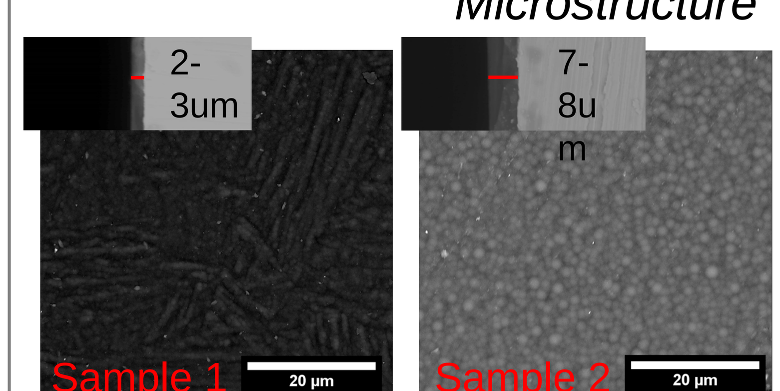
Results

Design of Experiment, DoE

Parameter	Sample 1	Sample 2
Gas Ratio (C_2H_2:H_2)	Low	High
Pressure	High	Low
Duty Cycle	High	Low
Process Time	Short	Long
Power	High	Low

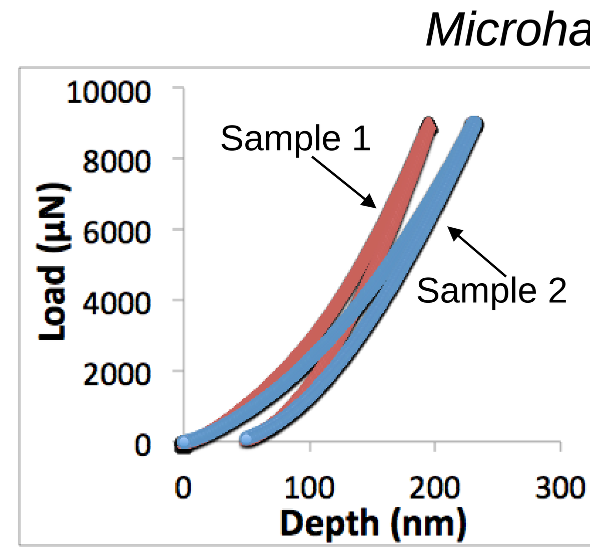
- Samples coated on steel substrate
- Rübig PN 70/90 contained inherent parameter interdependence
- Multiple synthesis parameters were varied simultaneously

Microstructure



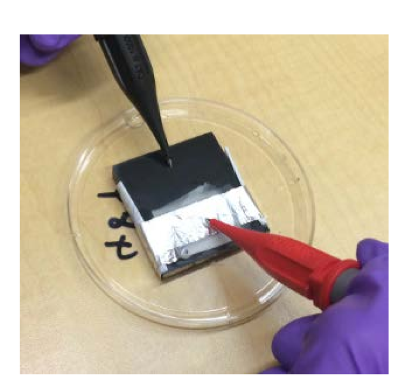
- Micrographs of DLC thickness overlayed on microstructure
- Sample 1 contained smaller grains

Microhardness



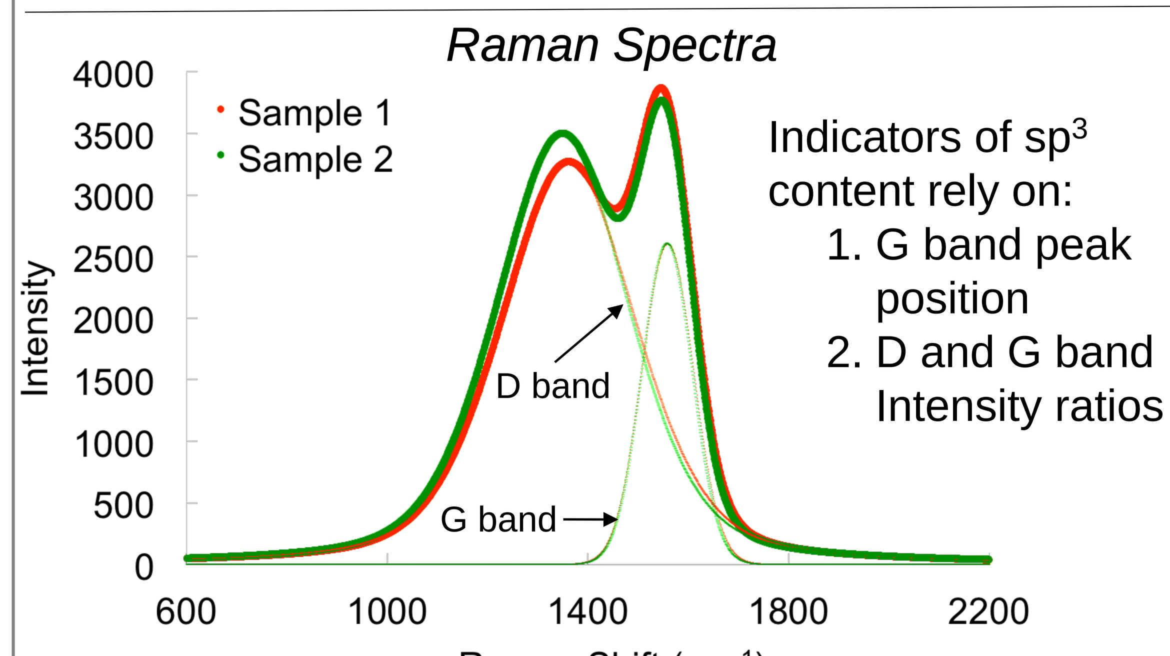
Sample	H (GPa)
Literature	5 – 49 [1]
1	10.9 ± 1.9
2	8.9 ± 0.9

Resistivity



Sample	Resistivity (MΩ)	Pass
1	0.03	NO
2	0.02	NO

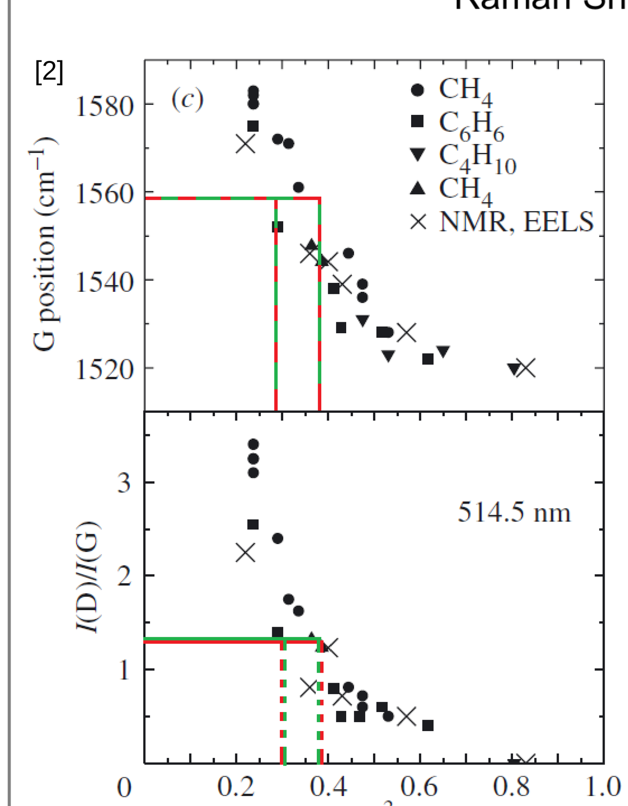
Raman Spectra



Indicators of sp^3 content rely on:

1. G band peak position
2. D and G band Intensity ratios

[2]



- The G band peak positions were too similar to distinguish between samples
- The D/G band intensity ratio showed Sample 1 containing more sp^3 carbon
- Both samples provided a qualitative range of sp^3 content (30-40%) for the PACVD synthesis parameters

Discussion

Characterization	Sample 1	Sample 2
Thickness	↓	↑
Grain size	↑	↓
Microhardness	↑	↓
Resistivity	↑	↓
sp^3 content	↑	↓

- While a single characterization technique could not distinguish samples, all techniques qualitatively indicated Sample 1 contained a higher sp^3 content

How did synthesis parameters influence sp^3 content?

Gas ratio → Increasing C_2H_2 gas should form more sp^3 due to more carbon (less hydrogen) involved in the synthesis
→ Not verified from samples due to:
1. Insignificant difference in gas ratio between samples
2. Other parameter changes outweighed effect

Pressure → Higher operating pressure should form a denser coating due to an increase in the number of effective collisions during synthesis [3].
→ Verified from samples

Process Time → A longer process time would extend overall exposure of reactants to substrate, increasing coating thickness
→ Verified from samples

Operating power → A higher operating power should increase ion energy during, increasing sp^3 content
→ Verified from samples

- Due to limited sample size and the parameter interdependence, quantitative conclusions were not found.

Conclusion

Material synthesis of a DLC coating relies on the understanding of PACVD instrument parameters. Based on the sample size, characterization techniques only began to distinguish the relationship between operating conditions and coating quality. Sample 1 surpassed sample 2 in hardness, resistivity, and sp^3 content. These qualities were most likely attributed to higher operating pressure and power. The differences that did exist were not significantly different but does not exclude the prevalence of these trends.

Recommendations

To increase sp^3 content, the relationship between the synthesis parameters and coating properties must be fully understood. A larger sample size should be used to independently test all parameters of the PACVD instrument.

References

[1] Prelas, M. (1998). The Hardness of Diamond. In Handbook of industrial diamonds and diamond films. New York: Marcel Dekker.
[2] Ferrari, A. (2004). Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond. Philosophical Transactions of The Royal Society, 1452, 2487-2487.
[3] Oliveira, É, Cruz, S., & Aguiar, P. (2012). Effect of PECVD deposition parameters on the DLC/PLC composition of a-C:H thin films. *Journal of the Brazilian Chemical Society,* 1657-1662.