Carbon Films for Corrosion Resistant Photoelectrochemical Cells

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Abstract— **Hydrogen represents an ideal source of clean energy, and a suitable power storage alternative. While there are many production methods available to produce hydrogen, they either use fossil fuels or suffer from low efficiency, detracting from any benefits this renewable energy source could provide. The purpose of this work is to fabricate a photoelectrochemical (PEC) cell that can use the energy of sunlight to power electrolysis to efficiently generate and capture hydrogen from water for use as fuel for applications such as mobile or stationary fuel cells. Most electrodes in modern PEC cells corrode fast, in less than a week, preventing the large-scale implementation of the technology. The research focuses on solving this issue by synthesizing Diamond-Like Carbon (DLC) through Plasma-Enhanced Chemical Vapor Deposition (PECVD) for use as an anti-corrosion layer and co-doping the film with Boron and Phosphorous atoms. The anticipated outcome of this work is to optimize the synthesis of DLC through PECVD and therefore to increase the lifespan of PEC cells to a range that is acceptable for industrial applications, without impeding the flow of electric current of the cell. We have shown that DLC can be synthesized at low temperature (~100°C) and the annealing enables the formation of diamond on the substrate. Moreover, the film experiences an increase in conductivity post phosphorous and boron implantation and annealing, demonstrating the effectiveness of the ion implantation method for the control of the conductivity of DLC films. The film characteristics were investigated by scanning electron microscopy (SEM), Auger Electron spectroscopy (AES), Raman spectroscopy and current-voltage (IV) measurements.**

Keywords — thin films, carbon, diamond, ion implant photoelectrochemical, hydrogen

I. Introduction

Hydrogen is the ideal clean energy source that can be used for fuel cells and automobiles [1]. Hydrogen can be easily obtained from the electrolysis of water, a highly abundant resource, while the energy producing reaction between hydrogen and oxygen has water as the only product.

Currently, hydrogen production is based on fossil fuel sources, such as steam reforming of CH_4 or coal gasification, that generate as much CO and CO_2 as the usual burning of the fuels [2]. It is, therefore, important to develop methods of H_2 generation that are truly Carbon-free to fulfil the promise of a clean, Hydrogen-based economy.

Using a photoelectrochemical (PEC) cell and solar light, hydrogen can be obtained by injecting electrons of appropriate energy to drive the spontaneous dissociation of water [3].

The main obstacle to the commercial expansion of the PEC's technology for hydrogen generation is that the photovoltaic (PV) absorber corrodes fast in a typical high pH electrolyte [5]. Nanocrystalline diamond-like-carbon (DLC) exhibits significant resistance against corrosion in electrolyte and is highly transparent as a thin film [4]. Applying a DLC thin film to an InGaN/Si PEC cell [5] has the potential to prevent the corrosion of its surface while allowing electrolysis to proceed [2].

II. Experimental Procedures

A. Plasma-Enhanced Chemical Vapor Deposition Setup

The PECVD is an in-house made system and consists of a stainless-steel reaction chamber connected to a gas flow control system that can supply the process gas (CH_4), the plasma gas (Ar) and the dilution gas (N_2). A turbopump, mechanical pump tandem ensures that the reactor can be efficiently pumped down to a base pressure of 10^{-5} Torr. The gas is allowed in the reaction chamber through a shower-head injector that ensures a uniform distribution of the precursor material across the sample surface. The substrate temperature is monitored with a thermocouple installed in contact with the sample susceptor and can be controlled between 100 ^{o}C and 600 ^{o}C. The reactor pressure is monitored using an ion gauge in the range of low pressures and a Baratron instrument for the pressure range from 0.01 to 760 Torr. An RF plasma generator with a frequency of 40 MHz is used to create argon plasma and for the enhanced generation of reactive CH_4 radicals.

978-1-5386-7755-1/18/$31.00 ©2018 IEEE

B. *Sample Fabrication*

All sample depositions were grown by PECVD deposition using CH_4 as a precursor gas for carbon and Ar as a carrier gas. The samples were grown on slide substrates of three different, materials: silicon (100), soda-lime glass, and quartz. The samples grown on the silicon and glass substrates were used to determine structural and optical differences between carbon films grown on crystalline and amorphous surfaces, respectively. Using the silicon and soda-lime glass samples, a set of single-factor experiments was designed to enable the optimization of the growth conditions with respect to CH_4 flow, reactor pressure and substrate temperature.

The samples grown on the quartz substrate were used for ion implantation and subsequent measurement of the electron properties. The quartz is a suitable substrate for high temperature processing, due its high purity (~17 ppm impurities) and low coefficient of thermal expansion while its high resistivity (Mohm·cm) allows simple measurement of the electrical properties of the DLC thin films.

The film growth was optimized using the growth rate (GR) as the experimental response and the highest value of the GR was selected as a measure of the optimal growth conditions. Two single-factor experiments were performed, selecting as experimental variables 1) methane flow with the following values: 5, 15 and 20 sccm and 2) reactor pressure with values of 700, 1400 and 2100 mTorr. The results of these experiments are depicted in figure 1 and 2 respectively. These samples were grown for 60 min at a nominal temperature of 100 ^oC and using a plasma generator frequency of 40 MHz with a power of 100 W, and an Argon flow of 20 sccm. Following these experiments, the optimal growth conditions were determined as 15 sccm for the methane flow and 1400 mTorr for the reactor pressure. All subsequent samples used for material characterization were grown under these conditions.

Two samples grown on quartz substrates have been used for ion implantation. The first sample has been implanted with phosphorus (P) with a dose of $1x10^{14}$ cm^{-2}, at an energy of 100 keV while the second sample was implanted with boron (B) with a dose of $1x10^{14}$ cm^{-2}, at an energy of 63 keV. Both samples have been annealed at 600 ^oC for 120 min.

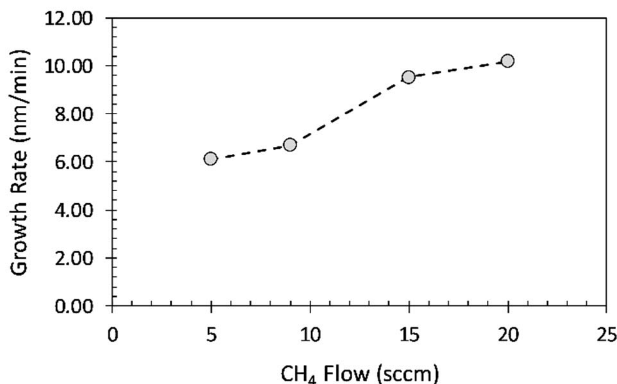

Fig. 1. Growth Rate as a function of Methane Flow

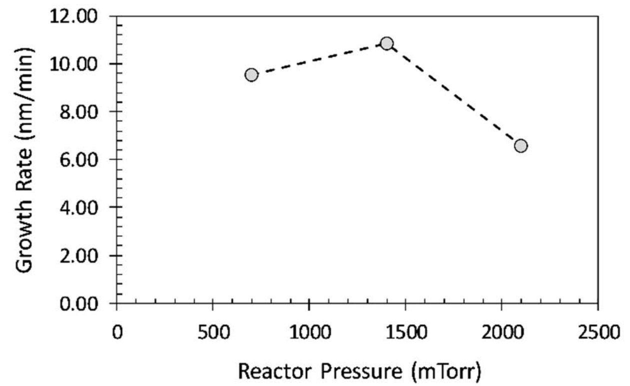

Fig. 2. Growth Rate as a function of Reactor Pressure

C. *Thin Film Characterization*

The diamond-like carbon films have been characterized by SEM to determine the film thickness, surface morphology and cross section properties. Raman spectroscopy has been used to determine the phonon spectra for the as-grown samples and for the samples annealed. Chemical composition of the films was investigated by X-Ray Photoelectron Spectroscopy (XPS), and Auger Electron Spectroscopy. The electrical properties of the DLC films before and after the ion implant and annealing were characterized by 4-point probe I-V measurements.

III. Results and Discussion

A. *Structural Characterization*

SEM images of the samples grown on silicon (100) substrate have revealed that the thickness of the films is in the range from 360 nm to 650 nm as a function of CH_4 flow and reactor pressure. All films are smooth and compact, with no visible voids or pit-holes, as shown in figure 3.

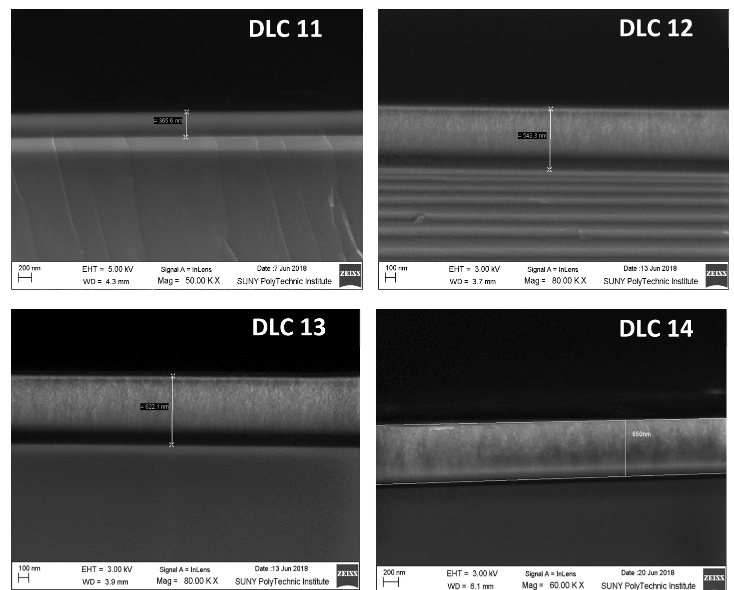

Fig. 3. LEO 1550 scanning electron microscope cross-sectional imaging of the samples grown on silicon (100).

The samples presented, DLC 11 – DLC 13 were fabricated with a varying CH_4 flow rate of 5, 15, and 20 sccm respectively at a pressure of 700 mTorr. DLC 14 was fabricated at a CH_4 flow rate of 15 sccm, but a pressure of 1400 mTorr.

Surface elemental composition and the compositional uniformity of the films, as a function of depth, were analyzed using Auger electron spectroscopy. AES is a technique that uses electrons with energies ranging from 50 eV to 3 keV to bombard the surface and trigger a chain of energy transitions between electrons on K-L-L shells ending with the ejection of an Auger electron. At these energies, the depth of penetration is only a few nanometers and thus the information collected represents the elemental composition of the surface of the material probed. AES, in conjunction with Ar^+ ion sputtering was used to determine the chemical depth profile of the carbon films deposited on quartz and on Si(100). The AES concentration profiles are presented in figure 4. Analyzing the depth profiles, it can be seen that C concentration for a typical sample grown on quartz has an average of 96.5% ± 0.5%. In these films, N concentration is found at an average of 2.1% while O concentration average is 1.3%. No silicon has been detected in the film. As the ratio of these elements is atypical for contaminants with atmospheric origin, their provenience has to be investigated further.

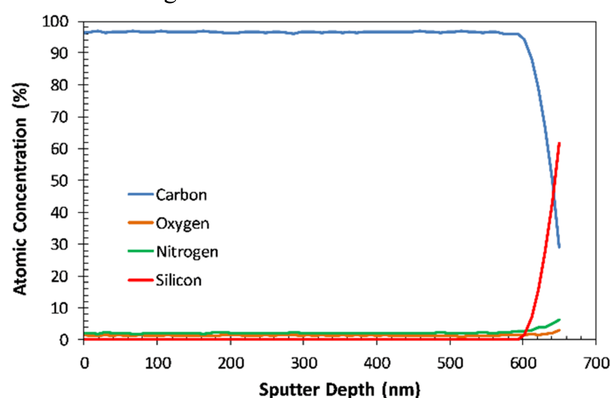

Fig. 4. AES depth profiles of optimized DLC samples deposited on quartz substrates.

X-Ray Photoelectron Spectroscopy (XPS) was used in addition to AES to analyze the composition of the material at the surface and the spectrum of an optimized sample grown on soda lime glass substrate is depicted in figure 5.

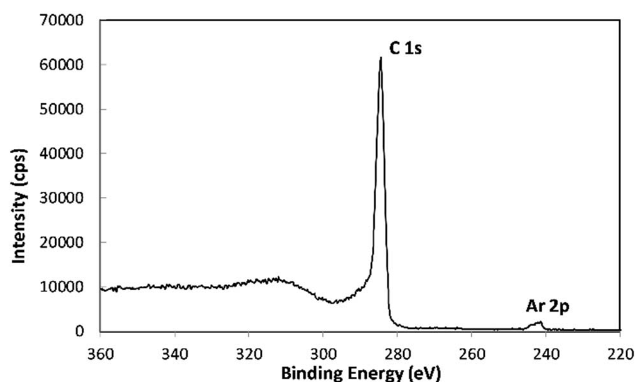

Fig. 5. XPS spectrum of after etching 10 nm below the surface.

The XPS spectrum was recorded using soft x-rays with photon energies in the range from 5 to 1200 eV to examine core-levels binding energies of the material. For the Carbon 1s electron level, the binding energy is 284.8 eV ±1 eV [6].

Argon (Ar) is the other element that could be expected to be part of the surface make up. The energy characteristic for the 2p electrons is 243.9 eV ±1 eV. The spectrum we measure exhibits a strong pick centered at 284.5 eV and another less intense peak at 241.1 eV. We associate these peaks with the carbon surface of the film and with the presence of Ar originating in the plasma plume.

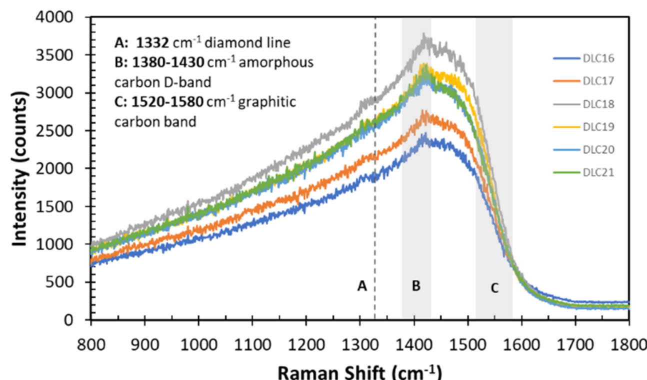

Fig. 6. Raman spectra of DLC films measured before ion implantation and annealing. Samples fabricated under identical parameters (20 sccm Ar, 15 sccm CH_4, 1400 mTorr) and on a soda-lime glass.

Raman spectroscopy has been found to be an accurate technique for the qualitative characterization of the carbon films. The films grown on glass slides have been characterized using UV laser excitation with a wavelength of 320 nm and the spectra obtained is presented in figure 6. According to the literature the feature at 1332 cm^{-1} can be assigned to a small fraction of diamond-like carbon, while the larger and wider peak is known as the D-band of the amorphous carbon. The intensity of the signal between 1520 and 1580 cm^{-1} is comparatively lower, suggesting that the fraction of graphitic carbon is low.

Annealing was performed on samples fabricated on quartz substrates and implanted with phosphorus. The annealing was performed at 600 °C for 120 minutes under an Ar flow of 150 sccm and a pressure of ~1.5 Torr. Following the annealing, the film was characterized by Raman spectroscopy to determine the structural changes that occurred, figure 7. A sharp peak was

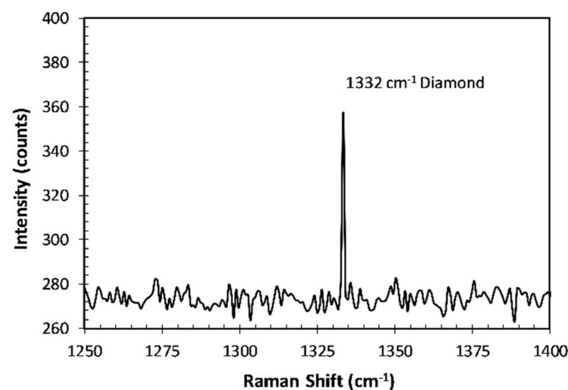

Fig. 7. Raman spectra of P-implanted DLC film after annealing.

found at the position characteristic for diamond (1332 cm^{-1}) while the graphitic and amorphous features have vanished completely.

B. Electrical Characterization

Current-voltage measurements were performed on the samples implanted with P and B. P-doping was found to produce a relatively deep donor with a level of 570 meV below the conduction band edge (CBE) of single crystalline diamond [7] while B-doping was found to produce an acceptor with a level of 370 meV above the valence band edge (VBE) [8].

After the samples were implanted, they were annealed at 600 °C for 120 minutes under argon flow as described previously. To determine the effect of implantation and annealing on the conductivity of the films, a 4-point probe measurement configuration was used to perform IV sweeps on the films from -10 to 10 V. Indium dots were used as contacts for the probes in order to ensure an ohmic contact.

The samples were measured, before and after implantation and annealing. As shown in figure 8, the typical as-grown sample is insulating, with practically no current measured across the voltage range.

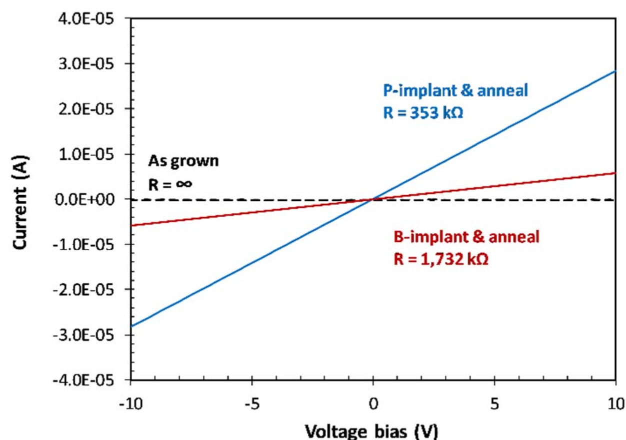

Fig. 8. IV sweep of samples fabricated on quartz substrate. Indium dots were used as contacts for each measurement.

After implantation and annealing we have found that the P-doped sample, exhibits electric conductivity with a resistance of 353 kΩ while the B-doped sample has shown a resistance of 1,732 kΩ. Both samples, demonstrate that despite the deep energy levels, the P and B atoms can be ionized and become effective donors and acceptors, respectively. Moreover, it was demonstrated that dopant atom densities in the range of 10^{14} cm^{-3} can produce a significant change of the conductivity. This promises that the ion implantation at increasing doses will produce a gradual and controllable change in the material conductivity. The ultimate goal of the doping process is to demonstrate the ability to control the Fermi level in the DLC films through co-doping with P and B.

IV. Conclusions

In a novel experiment, Carbon films were fabricated by PECVD and the process parameters were optimized using the maximum growth rate as indicator of the best growth conditions. While the films exhibited diamond-like properties such as no conductance and optical transparency, Raman measurement finds just a small peak at the location typical for sp^3 boding of diamond (tetragonal).

The sp^2 bonding peak corresponding to graphitic phase (trigonal planar) is not present, leading to the conclusion that graphitic phase is minimal. The dominant peak corresponds to the D-band that is associated with ta-C:H (Tetrahedral C, doped with H) [9,10].

After P-implant and annealing the amorphous carbon features have vanished and only a sharp peak indicating the presence of diamond-like carbon is found. It is therefore expected that the films will exhibit the properties of the polycrystalline diamond. After implanting the samples with a 10^{14} cm^{-2} dose of either Boron or Phosphorous, the films electrical properties changed allowing increased electric conduction through the film. This leads to the conclusion that an optimized implant dose could change the electrical properties of the film in such a way as to allow electric conductance while maintaining corrosion resistance of the diamond.

Acknowledgments

A special thanks to Steven Novak for assistance with AES analysis, Hassaram Bakhru for assistance with ion implantation, and Sandra Schujman for assistance XPS analysis.

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