Correlation of CN/C2 ratios in MicroWave Plasmas to Electronic Properties of Ultrananocrystalline Diamond Films.

Dieter M. Gruen, P. Bruno, Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439

The discovery of ultrananocrystalline diamond (UNCD) films, the third member of a remarkable triad of nanostructured carbons which includes fullerenes and nanotubes had its conceptual foundation in 1991 when a radically different plasma chemistry based on carbon dimmer, C2, as the growth and nucleation species was proposed.

UNCD thin films consist of 2-5 nm grains of pure sp^3-bonded carbon and 0.5 nm wide grain boundaries, with a disordered mixtures of sp^2 and sp^3 bonded carbon. Such a film have emerged as potentially revolutionary materials for use in electronics, microelectromechanical system (MEMS), or bioinert coatings and as wear resistant coatings. They in fact exhibit interesting properties that are the result of their unique nanoscale morphology and electronic structure.

It has been recently (1997) demonstrated that the addition of small amount of nitrogen to the methane/argon feed gas, has a profound impact on the film electrical conductivity, as well as it leads to an enhanced deposition rate, affecting the growth habit and altering the composition of the lattice sites. In particular, the HRTEM data indicated that the grain size and GB width increase with the addition of nitrogen, while transport measurement indicate that the electrical conductivity is increased dramatically with nitrogen incorporation, resulting in the highest known *n*-type conductivity of any diamond thin film. The creation of a useful, ambient temperature, highly conductive n-type UNCD is a breakthrough in diamond science. A high temperature all-diamond pn junction heterostructure diode has shown excellent rectification properties.

To obtain a better understanding in the change in structure and electronic properties upon nitrogen incorporation several attempts have been made which are not found beyond disputation. A possible explanation of that result comes from the fact that nitrogen introduces changes in morphology and electronic structure within the grain boundaries that may lead to enhanced electronic transport, since simulations indicate that the introduction of nitrogen into high-angle twist diamond grain boundaries is energetically favoured by 3-5 eV compared to substitutions into grains.

Previous works focused on the effect of the changes in the plasma chemistry on the film morphology and electrical transport properties as nitrogen is incorporated in to UNCD film pointed out that these properties are both greatly affected by the presence and

amount of CN in the plasma, which varies as nitrogen is added. The single effects of nitrogen addition observed in the plasma are in fact the emission of nitrogenous species excited states. With regard to this latest point, open questions still exist with respect to the production channel of CN and to its contribution in the thin film synthesis process.

A detailed study of CN/C2 ratios as a function of nitrogen content has been undertaken in our laboratory using Optical Emission Spectroscopy (OES) on plasma phase in the conventional MW CH_4-Ar-rich gas mixture successfully used for UNCD film deposition. OES spectra were recorded using a fixed Ar/CH_4 feed gas flow rate (100 sccm) with the addition of known quantities of nitrogen in the range 0-20 sccm. Efforts were made in these experiments to get the dynamics of the nitrogen incorporation in the initially pure Ar-methane discharges by obtaining data for a given set of power, pressure, methane concentration and temperature.

Previous measurement of the C_2 (d$\rightarrow$a) $\Delta v=0$ progression, recorded at higher resolution, showed no obvious variation in band contour with either process conditions or with spatial location, i.e. the emission intensity obtained from the integral of a vibrational band and from a fixed wavelength both follow the same trend with changes in the process conditions. This encourages the assumption that spatial variation in emission intensities, monitored via the intense (0,0) band head at 516 nm, are representative of the entire distribution of emitting C_2 species.
Moreover it has been correlated the emission observed from C2 with the absolute density of C2 through light absorption measurements on the same transition as the observed emission and pointed out a strong linear correlation between them. These results verified the use of Swan band emission as an indicator of C2 concentration and could be used for our purposes for following the emission lines behaviour detected by OES as a function of nitrogen addition in the feed gas, assuming therefore that the linearity could be maintained also for the CN radical.

The Ar-CH_4 emission spectra are dominate by the C2 (d$^3\pi_g\rightarrow$a$^3\pi_u$) Swan band system, although emission from atomic hydrogen (Balmer transition, henceforth H) is also visible.
The Ar-CH_4-N_2 plasma spectra also includes emission from the CN (B$^2\Sigma^+\rightarrow$X$^2\Sigma^+$) system (hereafter also referred to as CN (B$\rightarrow$X). CH (A$^2\Delta\rightarrow$X$^2\Pi$) emission is not clearly discernible, because it is too weak in comparison with the Swan band system or the CN (B$\rightarrow$N) system that is not considered in this study. All emission lines from argon (neutral or ionic), observed from the pure Ar plasma, are quenched on addition of nitrogen, thus preventing their use in actinometric measurements. Summarizing the wavelengths probed were the following ones: the (0,0) bandhead at 516.5nm for C2 emission; in the

case of the CN (B→N) the emission at 387 nm was collected, while H_a was monitored at 656.2 nm.

Throughout the OES studies the measurements of the emission intensities, taken as a function of the process conditions, were obtained at a fixed wavelength and not as the integral of the vibrational band. This method was chosen as the overlapping of visible emission from a number of species and vibrational systems complicates the spectrum.

We observed that both the densities of C2 and CN radicals are affected substantially as N2 gas is added, while their ratio changes as well. For small additions of N2 (1-4%), the effect is to increase the density of CN and decrease the density of C2 dimers. As the nitrogen content goes up to 5%, the relative density of C2 to CN increases again by a factor of 0.5. The growth observed in CN (B→N) emission clearly implicates nitrogen as a species that participles in the gas phase chemistry. CN is seen as a stable discharge species, which once created maintains its identity in terms of line intensity. It was also observed that the CN emission band intensity follows the pattern of increase of C2 as a function of nitrogen addition for higher (> 5%) nitrogen content. These features indicate the production of CN molecules in the multi-component plasma comprising N_2, Ar and CH_4 due to reactions between C2 and N_2 with Ar acting as a regenerative carbon agent. C2 is mainly introduced in the discharge by the dissociation of the C_2H_2 and his behaviour as nitrogen is added to the feed gas (decrease up to 5sccm of N_2 and then increase) reflects the thermo-chemical quenching induced by the addition of just trace of nitrogen. At higher nitrogen addition its trends could be explained in terms of an additional chemical equation regenerating the carbon specie.

A thermo-chemical analysis is proposed in order to elucidate the intrinsic relationship existing between the plasma chemistry and the film properties. The most likely main chemical pathways involved in these plasmas are discussed and an appropriate reaction scheme is proposed.

References
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