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DOPING OF NANO-SIZED DIAMOND LIKE CARBON FILMS AND THEIR CHARACTERIZATION BY MICRO RAMAN SPECTROSCOPY

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Abstract: Capabilities of the rf plasma beam source in deposition of ultra thin diamond like carbon for the hard disk drive applications have been studied. Nano-sized films were doped by nitrogen, hydrogen and silicon and characterized by micro Raman spectroscopy. Projected ranges of incident carbon ions into the magnetic layer as well as growing film were calculated by Monte Carlo simulation. Ion ranges at 100 eV incident energy were around 0.5 nm. With micro Raman spectroscopy is possible to qualitatively determine optimal deposition parameters and to follow changes in the film properties and carbon binding structure in amorphous matrix with hydrogen, nitrogen and silicon doping elements.

Keywords: diamond like carbon, Raman spectroscopy, plasma beam source, ultra thin film.

1. INTRODUCTION

Diamond like carbon (DLC) films doped with hydrogen, nitrogen and silicon in thickness range 1-4 nm must possess several properties for the hard disk drive applications: uniformity in thickness distribution higher than 5% over a 10-cm diameter, void-free structure, wear resistivity, corrosion protection and desired bonding to the lubricant topping [1-4]. Plasma and ion beam deposition techniques are the only deposition methods that can provide these film properties. Various hydrocarbons with hydrogen and nitrogen have been used as a carbon and doping elements precursor. Silicon can be provided either through the gaseous state or as a result of concurrent Ar/Xe ion beam sputter deposition from the separate Si solid target. During the film growth incident ion energies of carbon ions and doping elements were around 100 eV. In order to achieve good film adhesion, the projected range of carbon ions into the common CoCrPtB magnetic underlayer must be above 0.5 nm at the very beginning of the film growth. The projected ranges of doping elements into the magnetic layer as well as into the growing DLC film in the energy range 100 - 1000 eV are usually estimated by Monte Carlo method. Doping elements in the DLC film can be used for the film properties adjustments:

a) Hydrogen: lubricant displays more mobile characteristics since the sp^3 formation takes place not only among the C-C bonds but also among the parallel formation of C-H bonding network; Hydrogen passivates, terminates inactive sites on the carbon surface; lower film density.

b) Nitrogen: Higher atomic density (up to 2.2 g/cm^3), better lubricant bonding; better tribological properties with respect to micro-scratch

c) Silicon: Extremely low friction, stability against humidity, lower surface roughness and good adhesion strength. A slight decrease in the film hardness has been measured with Si doping. Good bonding characteristics toward PFPE molecules [5].

d) Fluorine: Better friction performance, good wear durability.

Taking into account the central carbon atom and its first three neighbors we can talk about the DLC film micro-crystallinity in the short domain range, up to 0.5 nm. Aside from the possible independent rf or dc bias of the substrate, the plasma and ion beam technologies are preferred tools in adjust-

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ment the projected ranges of dopants and overall DLC film quality. Using the micro Raman spectroscopy, the characteristic carbon peak shifts, band widths and area under the convoluted the G and D- band were measured. It is possible to qualitatively measure the presence of doping elements, binding configuration among carbon atoms and check the repeatability in the film structure for various deposition conditions. Micro Raman spectral area was between 1050 and 2000cm^{-1} with initial peak adjustments of Raman G and D peaks at 1555 and 1380 cm^{-1}, respectively. Vibrational excitation of the carbon atoms in the hexagonal plane arrangement depends also on the incident energy of Raman laser irradiation. The Ar laser light at 514 nm was used in evaluation of DLC films deposited by plasma beam source and a filtered cathodic arc source used for DLC films with Silicon doping.

2. EXPERIMENT

The beam size at the extraction net was 130 mm and the current density was up to 1 mA/cm^2. At the beam throw distance of 14 cm typical DLC film deposition rates were between 3.6 and 5.2 Angstrom/s for the incident rf power input in the range of 300 -700 W. The energy of incident ions in the plasma beam was measured by retarding field analyzer. The beam energy can be varied either by imposing the substrate bias or by changing the self-bias potential at the extraction grid of rf source, Figure.1. During one rf cycle the extracted beam is effectively neutral since the same amount of electrons and ions were extracted from the plasma. There may be a slight change in the substrate bias potential due to the different coefficients of secondary electrons emissions for incoming ions on CoCrPtB substrates and the growing DLC film.

The rf power used was up to 1000 W at 27 MHz. The source has reactive gas operation capability with low energy, high current plasma beam, and capability for surface treatment of electrically insulating materials.

Radial profile of ion beam current can be adjusted by magnetic fields produced by electromagnetic coils either in parallel or hyperbolic arrangements. Stainless-steel grid transparency is 70%. The DLC film deposition rate and its uniformity depend on the "beam throw distance", Figure 2. Plasma ions are neutralized by collisions with residual gas. The RF plasma beam source capabilities have been evaluated for the given reactor geometry, ethylene gas and available vacuum pumping setup, Figure 3. Ion current of the plasma beam was measured with a RF shielded Faraday cup. Voltage on the suppression electrode was –75 Vdc with orifice diameter of 0.1 mm.

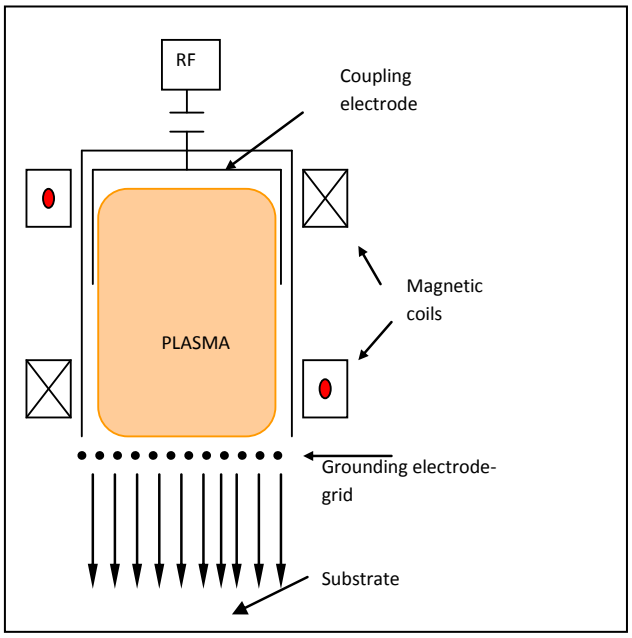

Figure 1. Plasma beam source Magnetic field: up to 280 Gauss per coil. 2 DC power supplies. Spark igniter. Extraction net: tungsten, 0.1 mm wires,1 mm net.

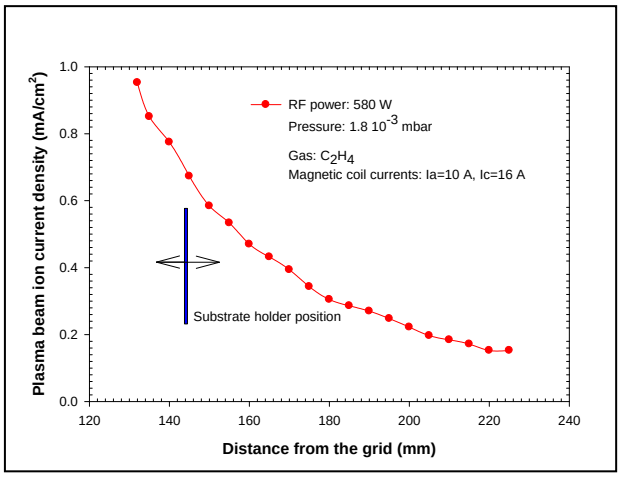

Figure 2. Dependence of the ion current density with the "beam throw distance". Other plasma parameters were kept constant.

The coupling and extraction electrode of the plasma beam source were made from stainless-steel and tungsten, respectively. Both materials are prone to DLC deposition, i.e. self- contamination.

Any replacement of the carbon containing working gas by Ar or any other gaseous dopant, at the beam constant operating pressure, leads to the drop in DLC film deposition rate, Figure 4. Dopant energetic ions, H and N recombine easily on the substrate surface and in molecular form desorbed, leave a chamber by the pump action.

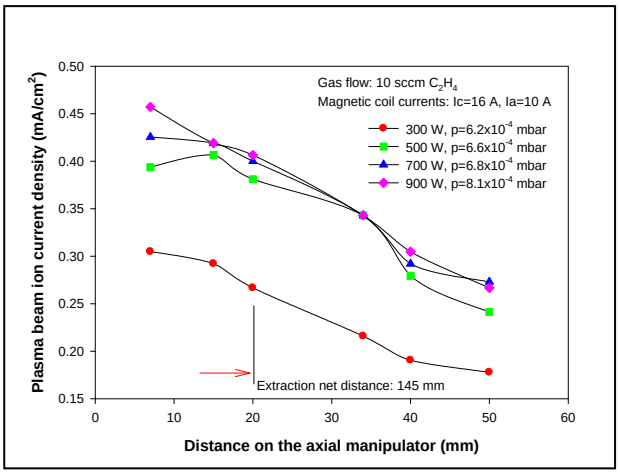

Figure 3. Dependence of the plasma ion current density versus delivered rf power with gas pressure as a parameter.

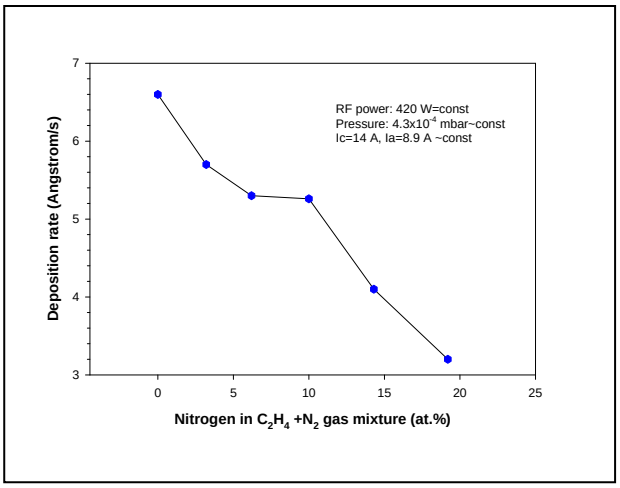

Figure 4. Dependence of the DLC film deposition rate versus the gas composition mixture. In the plasma beam chamber the gas pressure was kept constant.

Deposition rates of a-C:H:(N) films can be in the range 4 -10 Angstrom/s. The hydrogen content in a film follows an increase in the applied rf power. Film properties vary with applied rf power i.e. extracted ion energy. From the source calibration data, extracted ion energy versus implemented rf power, the maximal percentage of sp^3 carbon coordination can be expected at the rf power of 450 W. This power should correspond to the extracted ion energy of ~95-100 eV/carbon ion [6, 7].

In pure ethylene plasma the ion current density of the plasma beam is in the range 0.2 - 0.7 mA/cm^2 at the beam throw distance of ~14.5 cm.

For the rf plasma beam source there is a simple relationship between the area of the electrodes and the extracted ion energy, being proportional to the grid self bias potential.

$$Usb_1 / Usb_2 = (A_2 / A_1)^n \quad (1)$$

With $1 \leq n \leq 4$

Usb_1 – self bias potential on the capacitively coupled electrode

Usb_2 –self bias potential on the extraction electrode, grid.

3. RESULTS AND DISCUSSION

In order to compare different intensities of the inelastic scattered light from the DLC surface, on all investigated samples the same optic magnification, transmission of Ar laser light at 514 nm and a beam spot size, 4-5 micrometer in diameter, with sharp edges were selected. Also, a care has been devoted to select an ultra smooth portion of the DLC film.

The broad carbon spectrum, Figure 5, can be deconvoluted with the "distorted" D peak, "graphite" G peak and the peak remaining portion, slope, which corresponds to the amount of embedded hydrogen atoms within the DLC matrix. Also, other parameters like area under these peaks, peak widths at their half maximum for their fitted Gaussian profile are useful in the qualitative study of DLC films deposited at different plasma parameters.

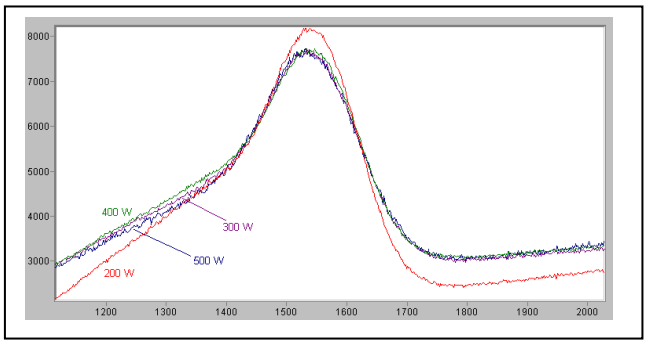

Figure 5. Overall Raman spectrum in the wavenumber region 1050-2000 cm^{-1} of plasma beam deposited a-C:H films at different RF power discharges, i.e.-ion beam energies.

With an increase of the ion film deposited energy there is a change of the bonding angle and lengths among carbon atoms in the graphite hexagonal ring. Area under the "distorted" D peak becomes larger and the shifts of the peaks go through their maximum. An upward trend of these shifts has been presented in Figure 6. With a further increase of RF power the width of the G-peak starts to increase and the Raman shifts of the D and G peaks begin to decline.

Other macro study of DLC film properties, like nanohardness, and internal stress point out that at this rf power, corresponding to carbon ion energy of approximately 100 eV, the maximum of sp^3 coordination among carbon atoms is to be expected.

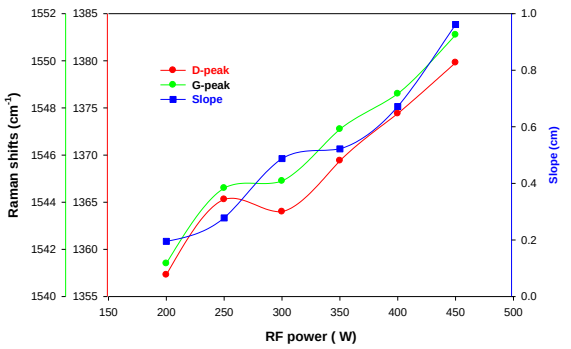

Figure 6. With increasing the RF discharge power there is an increase of the extracted ion energy of the plasma beam. The upward trend in the G and D peak position reaches its maximum at about 450 W RF power.

Doping of DLC films with nitrogen, by increasing the nitrogen atomic concentration in ethylene and nitrogen gas mixture, for other plasma parameters kept constant, show the similar upward trend in the D and G peaks shifts. Figure 7.

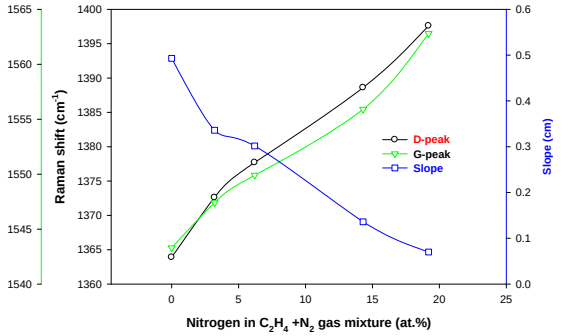

Figure 7. Positive constant shifts of the Raman deconvoluted D and G peaks with increase of the nitrogen atomic concentration in the gas mixture.

The fitted linear slope in the region 1050-2000 cm-1 (below the carbon signal) indicates a smaller amount of hydrogen incorporated in a film. Doping of DLC films with silicon (either by simultaneous Si sputtering from the solid target or concurrently embedding silicon chips in the filtered cathodic arc source) leads to the increase of carbon tetrahedral coordination within the DLC film. Si is unable to form double bonds and promotes creation of the sp^3 regions in the carbon network [5].

Monte Carlo simulation of the film growth

In order to make dense, smooth and pinhole-free film it is necessary to change the incident ion energy of the film forming species during the DLC film growth. Aside from small hydrogen atoms that penetrate easily into the CoCrPtB magnetic layer, the range of carbon and nitrogen ions is limited to 0.5 nm and 0.6 nm for the incident energies of 100 eV and 200 eV, respectively, Figure 8. Similar simulation for the range of carbon ions at 100 eV has been conducted for the carbon growing film composed of a-C:N (5 at.%N), ta-C:N (5 at % N) and graphite. Calculated range of C ion (100 eV) was 8.5, 4 and 6 Angstrom, respectively.

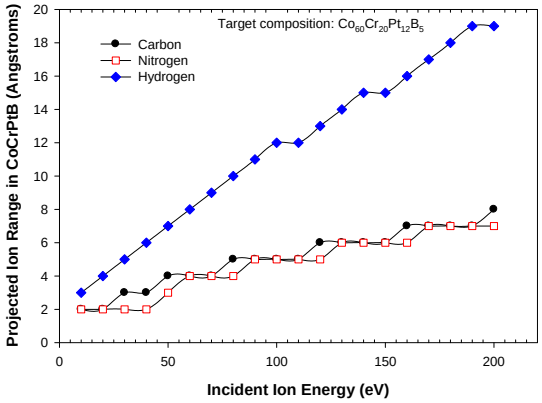

Figure 8. Monte Carlo simulation of the range of C, N and H ions in the energy range 10-200 eV into CoCrPtB layer.

4. CONCLUSIONS

Evaluation of the RF plasma beam source capabilities has been conducted for the given reactor geometry, ethylene gas and available vacuum pumping setup. Deposition rates of a-C:H:(N) films can be in the range 4-10 Angstrom/s. With micro Raman spectroscopy under constant and repeatable deposition conditions of DLC films doped with different elements it is possible to qualitatively evaluate film properties, percentage of doping elements. Interface width, overall surface roughness, mixing of the layers can be controlled by the proper selection of the incident ion energies and their impact angles. The hydrogen content in a film follows an increase in the applied RF power.

5. ACKNOWLEDGMENT

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ДОПИРАЊЕ ДИЈАМАНТУ СЛИЧНИХ УГЉЕНИЧНИХ ФИЛМОВА НАНОМЕТАРСКЕ ДЕБЉИНЕ И ЊИХОВА КАРАКТЕРИЗАЦИЈА ПОМОЋУ МИКРО РАМАНОВЕ СПЕКТРОСКОПИЈЕ

Сажетак: Проучаване су способности rf извора плазменог снопа при наношењу ултратанког угљеника сличног дијаманту за апликације јединица хард диска. Филмови нанометарске дебљине допирани су водоником, азотом и силицијумом и извршена је њихова карактеризација помоћу микро Раманове спектроскопије. Процијењене дубине продирања јона угљеника у магнетном слоју и у растућем филму су добијене уз помоћ Монте Карло симулације. Опсези јона при 100 eV упадне енергије били су око 0,5 nm. Помоћу микро Раман спектроскопије могуће је квалитативно процјењивати оптималне величине наношења и пратити промјене карактеристика филма као и структуру везивног угљеника у аморфној матрици са допирајућим елементима, одн. водоником, азотом и силицијумом.

Кључне ријечи: дијаманту сличан угљеник, Раманова спектроскопија, извор плазменог снопа, ултра танки филм.