# Carbon Film Deposition in Hydrocarbon Plasma Produced by Ribbon Electron Beam at Fore-Pump Pressure

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Abstract - Electron gun, which produces ribbon like beam in fore-vacuum pressure range, was applied for plasma chemical carbon films deposition. Electron beam with 2-3 keV energy was propagated in propane at pressures 5-10 Pa. Gas dissociation took place in created plasma. Reaction products were deposited on substrates, which were placed in this plasma. Deposition rate was detected to be non monotonically depended on distance between substrate and beam symmetry plane. Maximum of this dependence is proposed to be due to existence of two contradictory mechanisms, one of which assisted to film growth and the other prevents it from. Proposed model is based on hydrocarbon radicals flow and ion etching as the most probable mechanisms.

#### 1. Introduction

Plasma chemical reactions are widely used for different films deposition. Techniques, applied nowadays for these aims, are mainly based on different type discharges as electrode as electrode less. All these methods have a number of disadvantages. Main of them are: impossibility of uniform plasma production at large (about 1 m<sup>2</sup>) area, absence of sharp plasma boundary, difficulties with large (several kW) power input in plasma, that in its turn limits reaction and films deposition rates. In this work plasma was created by electron beam, propagating in hydrocarbon gas. Beam was produced by new type electron gun [1] which is able to generate ribbon like beam at pressures 5-10 Pa, which are high enough for satisfactory reaction rates. The objective of present work was to show possibility of ribbon electron beam application for plasma chemical carbon films deposition and to investigate film properties as function of deposition parameters.

## 2. Experimental Set-Up

Scheme of installation is shown at Fig. 1. It includes electron gun, consisted of hollow cathode 1, plane anode 2, accelerating electrode 3. Magnetic field, directed along beam, served for beam focusing and plasma confining. Beam was collected by electrode 4. Reaction products were deposited on substrates 5. There were also two power supplies for discharge and accelerating systems. Discharge current  $I_d$  was controlled during experiments. Gaseous propane was in-

serted directly in vacuum chamber. Details of experiment on films deposition are shown at Fig. 2. Electron gun 1 produces ribbon beam 2. Polished glass and silicon substrates 3 were displaced at different distances *X* from middle beam plane. Film thickness was measured by micro interferometer and film hardness by Nanohardness Tester NHT-S-AX-000X.

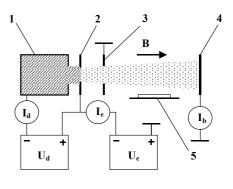


Fig. 1. Scheme of installation

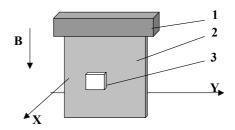


Fig. 2. Scheme of experiment on films deposition

### 3. Results and Discussion

As it was shown earlier [2], one of the main problems in ribbon beam producing in fore-vacuum pressure range is beam non uniformity. Investigation of this non uniformity reason allowed to produce beam 250 mm wide with not more than 10% current density variation along Y axis (Fig. 2) [3]. Along X axis plasma density is approximately Gaussian. It was important to know film deposition rate as a function of X coordinate. For this purpose we used substrate holder which contained substrates at different X. Fig. 3 presents dependence we searched. This dependence is non monotonous. Deposition rate decreases slowly with X growth and sharply falls at small X. Maximum position moves to higher X if beam current grows. To explain this curves we proposed two main processes. One of them is film growth due to hydrocarbon radicals flow and other is film etching because of ion sputtering. For these ions energy estimation we measured both plasma and floating substrate potentials. Results are presented at Fig. 4,a,b). For all distances X substrate floating potentials are negative and grow with X increasing, and plasma potentials are positive and fall with X. Potential differences  $\Delta \varphi$  are more at small X (Fig. 4,c).

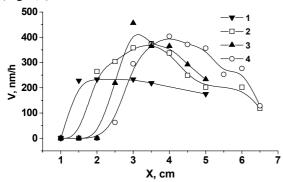


Fig. 3. Film deposition rate as a function of X coordinate for different beam currents  $I_b$  (1 - 100 mA, 2 - 200 mA, 3 -300 mA, 4 - 400 mA)

It qualitatively explains deposition rate falling at small X, because as more  $\Delta \varphi$  as more ion etching rate of growing film. To provide quantitative estimations we proposed model based on two abovementioned processes. In this case radicals flow  $j_r$  may be wrote as

$$j_r = n_r \cdot u_r \,, \tag{1}$$

where  $n_r$  – radicals density and  $u_r$  – their thermal velocity. We took into account that radicals appear owing to beam electron interaction with gas molecules. Radicals motion is diffusion, their recombination is possible. It allowed to write down one dimensional un interruption equation

$$-D_r \cdot \frac{d^2 n_r}{dx^2} = \frac{j_b n_0 \sigma_{re}}{e} - \gamma \cdot n_r^2, \qquad (2)$$

where  $D_r$  – radicals diffusion coefficient,  $j_b$  – beam current density,  $n_o$  – gas molecules concentration,  $y_r$  – radicals formation cross-section,  $\gamma$  – radicals recombination factor. For etching rate estimation we used formula

$$u_{\text{etch}} = n_i \cdot u_i \cdot k, \qquad (3)$$

where  $n_i$  ion density in plasma,  $u_i$  – thermal ion velocity, k – sputtering coefficient. It depends on energy as  $k = k_0 e^{\alpha \Delta \varphi}$ , where  $k_0$ ,  $\sigma$  – empirical coefficients. Function  $n_i(x)$  was found experimentally. Calculated flow densities of depositing radicals for different beam currents are presented at Fig. 5. As it can be seen, left side of maximum moves toward more X if beam current increases. Of course, several constants (sputtering coefficients, for example) are not known exactly. Therefore, results of calculation serve in great degree for estimation. At the same time coincidence of character of calculated and experimental dependencies and the order of calculated values are reasonable enough to consider proposed mechanisms as taking place in reality.

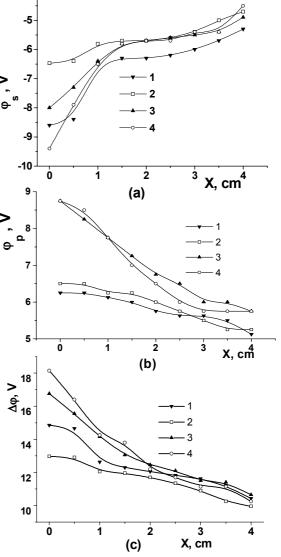


Fig. 4. Floating substrate (a), plasma (b) potentials and potential difference (c) as functions of X coordinate for different beam currents: 1 - 100 mA, 2 - 200 mA, 3 - 300 mA, 4 - 400 mA

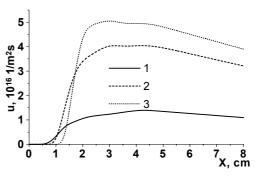


Fig. 5. Calculated depositing radicals flow density for different beam currents: 1-100 mA, 2-300 mA, 3-400 mA

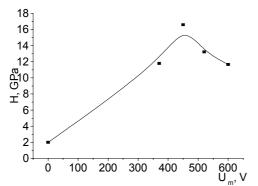
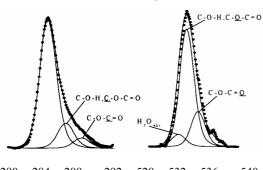


Fig. 6. Films hardness H as function of negative pulse bias voltage U (frequency 30 KHz, pulse duration 100  $\mu$ s, P = 45 mTorr Propane)



280 284 288 292 528 532 536 540 Bonding energy, eV

Fig. 7. XPS spectra of carbon films (Carbon content up to 88.5%)

As it was mentioned above, hardness of prepared carbon films was measured. When silicon plates were used as substrate, it was possible to apply pulse negative bias to substrate. Films hardness as function of pulse negative bias voltage are presented in Fig. 6.

As it was expected substrate negative bias increases film hardness owing to ion bombardment. XPS spectra of prepared films showed oxygen presence (Fig. 7). We suppose, source of oxygen is residual gas atmosphere of vacuum chamber.

Possible application of prepared films may be protective coatings for glass and plastic.

#### 4. Acknowledgements

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## References

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