

Particle Simulation of CH₄/H₂ RF Glow Discharges for DLC Film Deposition

B. Farouk and K. Nagayama[@]

Department of Mechanical Engineering and Mechanics

Drexel University

Philadelphia PA 19104

Telephone: 215 895 2287; Fax: 215 895 1478; e-mail: bfarouk@coe.drexel.edu

PACS numbers: 52.75.R Plasma applications in film deposition, 52.65 Plasma simulation,
81.15.G Plasma assisted CVD

ABSTRACT

Particle-in-cell/Monte Carlo (PIC/MC) simulations of capacitively coupled radio-frequency (RF) glow discharges were carried out for low pressure CH₄/H₂ plasmas. The present computational scheme considers the motions and collisions of both neutral and charged particles. The CH₄/H₂ plasma is modeled by combining a one-dimensional PIC/MC method with a polyatomic particle collision scheme. The model considers the motions of neutrals CH₄, CH₃, C₂H₃, H₂, and H, positive ions (CH₄⁺) and electrons. Space and time dependent results show that ionization rate is high at the sheath region. Deposition rate of carbon film is calculated by sampling impinging particles at the powered electrode. When CH₄ flow rate is decreased and the H₂ flow rate is increased, the gas density in the chamber and deposition rate decreased significantly for carbon containing radicals. On the other hand, when CH₄ flow rate is fixed and H₂ flow rate is increased, deposition rate again decreased, but the gas density in the chamber did not change much.

INTRODUCTION

Diamond like carbon (DLC) films deposited by various glow-discharge processes have properties much like those of diamond. DLC films are extremely hard, chemically inert, electrically insulating, and good thermal conductors¹. Many application areas have been suggested such as spacecrafts and heat sinks in electronic packaging. The role of hydrogen in vapor-activated deposition of diamond has been the focus of much attention^{1, 2} because only after excess hydrogen was used in these processes, that mm/h growth rates were possible. The role of hydrogen is significant in both gas phase chemistry and surface chemistry for these deposition processes. In gas phase chemistry, atomic hydrogen promotes the gas phase production of growth precursors, and suppresses the formation of polyatomic hydrocarbon species (PAHs) by molecular hydrogen². PAHs may be precursors to unwanted sp² carbon during the vapor-deposited DLC growth. Regarding surface chemistry, several factors such as

[@] Present address: Sumitomo Electric Industries, Ltd., Yokohama, Japan

REPORT DOCUMENTATION PAGE

Form Approved OMB No.
0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 09-07-2000	2. REPORT TYPE Conference Proceedings	3. DATES COVERED (FROM - TO) 09-07-2000 to 14-07-2000
---	--	--

4. TITLE AND SUBTITLE Particle Simulation of CH ₄ /H ₂ RF Glow Discharges for DLC Film Deposition Unclassified	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S) Farouk, B. ; Nagayama, K. ;	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Mechanical Engineering and Mechanics Drexel University Philadelphia, PA 19104	8. PERFORMING ORGANIZATION REPORT NUMBER
--	--

9. SPONSORING/MONITORING AGENCY NAME AND ADDRESS AOARD Unit 45002 APO AP, xx96337-5002	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
A PUBLIC RELEASE

13. SUPPLEMENTARY NOTES
See Also ADM001341, Rarefied Gas Dynamics (RGD) 22nd International Symposium held in Sydney, Australia, 9-14 July 2000.

14. ABSTRACT
Particle-in-cell/Monte Carlo (PIC/MC) simulations of capacitively coupled radio-frequency (RF) glow discharges were carried out for low pressure CH₄/H₂ plasmas. The present computational scheme considers the motions and collisions of both neutral and charged particles. The CH₄/H₂ plasma is modeled by combining a onedimensional PIC/MC method with a polyatomic particle collision scheme. The model considers the motions of + neutrals CH₄, CH₃, C₂H₅, H₂, and H, positive ions (CH₄⁺) and electrons. Space and time dependent results show that ionization rate is high at the sheath region. Deposition rate of carbon film is calculated by sampling impinging particles at the powered electrode. When CH₄ flow rate is decreased and the H₂ flow rate is increased, the gas density in the chamber and deposition rate decreased significantly for carbon containing radicals. On the other hand, when CH₄ flow rate is fixed and H⁺ flow rate is increased, deposition rate again decreased, but the gas density in the chamber did not change much.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:	17. LIMITATION OF ABSTRACT Public Release	18. NUMBER OF PAGES 8	19. NAME OF RESPONSIBLE PERSON Fenster, Lynn lfenster@dtic.mil
---------------------------------	--	--------------------------	--

a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	19b. TELEPHONE NUMBER International Area Code Area Code Telephone Number 703767-9007 DSN 427-9007
---------------------------	-----------------------------	------------------------------	--

etching, covering of the dangling bonds of surface carbons, removing hydrogen from surface C-H bonds (to create active growth sites) are affected by atomic hydrogen.

The role of hydrogen in DLC deposition process in pure methane plasma is not clearly understood¹. Most of the reported models for DLC deposition process are for pure CH₄ plasma³⁻⁸. These models focused on gas phase chemistry and surface chemistry rather than discharge kinetics. Rate equations with gas phase chemistry or plug flow model (simplified fluid model) were used to predict the number densities, etc. Electron energy, which determines ionization and dissociation rates, was obtained either by experimental data or via Monte Carlo simulation of electron kinetics. Depositions were predicted using sticking coefficients. A self-consistent fluid model for CH₄ plasma, using Boltzmann equation solver for DC field calculation of the electron energy distribution function was later developed⁹. The radical densities for CH₃ and CH₂ were calculated, however, these profiles did not compare well with experimental data. Hybrid models have also been developed and applied to RF plasma with gas mixtures^{10,11}.

In this study, we applied the PIC/MC method to simulate CH₄/H₂ plasmas in a capacitively coupled RF reactor. The model considers the motions of CH₄, CH₄⁺, CH₃, C₂H₅, H₂, H and electrons. Both flow rates and gas compositions or pressure were varied. The results are analyzed by comparing the power consumed, current flow, and the electron energy and density (at the center of the plasma) as the gas compositions are varied. Ionization and dissociation rates and the species densities are computed as functions of the gas composition and flow rates. The energy of the impinging ions to the cathode, and deposition rates are also obtained. The developed computational model will allow us to predict the carbon film deposition rate and its quality when different CH₄/H₂ compositions are fed into low pressure plasma assisted CVD reactors.

MODEL DESCRIPTION

The models used here are an extension of the one dimensional self-consistent particle model for capacitively coupled RF glow discharge of pure CH₄¹². A parallel plate configuration of the reactor is considered where the two electrodes have large cross-sectional areas compared to their separation distance, so that a one-dimensional approximation is valid for characterizing the discharge. The model considers motion and collisions of neutrals as well as of charged particles. To simulate the CH₄/H₂ plasma, we combine the particle simulation model with neutral motion and a polyatomic particle collision model which was developed in the rarified gas dynamics area^{13, 14}. For stable neutral/radical and radical/radical collisions, energy after collision is determined by the Borgnakke and Larsen¹⁴ model. In this model, both the relative translational and the internal energies are assumed to be distributed according to the respective equilibrium distributions and, at each collision, new values are sampled at random from

these distributions, subject to the condition that the total energy is conserved. Hence vibrational-vibrational and vibrational-translational energy exchanges are considered for the neutral/neutral collisions.

The model uses polyatomic particle collision scheme, which has been developed in the non-plasma area. Gas phase chemistry is considered by simplified reactions¹² to reduce the number of species in the particle model. In our particle simulation, we simplified the chemistry model of Kline et al.⁴ Electron-electron, electron-ion, and ion-ion collisions are neglected in the present study, as the probability of such collisions are small in weakly ionized plasma. For neutral-electron collisions, elastic scattering, excitation, and ionization collisions are considered. In each collision process total momentum is conserved. Total energy of collision pairs in elastic collision is preserved, while energy is lost in excitation and ionization processes. For the discharge kinetics, elastic scattering between neutrals are considered and electron impact to CH₄ and H₂ are considered. Hydrogen ion is neglected because the density is negligible compared to that of CH₄⁺ in the simulated range of parameters. Following gas-phase reactions are considered for the plasma:



Surface reactions considered in the present analysis are as follows:



Further details of the gas-phase and surface reactions considered can be found in Nagayama et al.¹². The depositing species are CH₄⁺ and CH₃ and C₂H₅ radicals. The deposition of hydrogen radical is neglected in this study. Film growth rate is predicted by sampling depositing particles on the surface using sticking probability. Sticking probabilities are assumed to be 1.0 for the ions and 0.1 for the radicals. Although the model does not consider a detailed surface model, it provides useful information for plasma physics and can identify major species impinging to the substrate.

For the present PIC/MC scheme, the reaction rates depend on the respective cross sections. In general, rate constant for any reaction is related to the cross section for that reaction as

$$K = \int_0^{\infty} f(E) \sqrt{\frac{2E}{m}} \sigma(E) dE$$

where E is the total energy of the collision pair, $f(E)$ is the energy distribution function, m is the reduced mass¹⁵ of the collision pair and $\sigma(E)$ is the cross section. For electron impact ionization or dissociation, cross section area is expressed as a function of electron energy¹⁶, which is directly used in PIC/MC simulations. No electron-impact excitation reactions were considered in this study. For neutral stable/radical and radical/radical reactions, rate constant must be transformed to cross section σ as PIC/MC method requires cross section area as input data. Assuming hard sphere model¹⁵, the above equation can be solved for $\sigma(E)$ as

$$\sigma(E) = K \sqrt{\frac{m}{2E}}$$

In order to get stable results with a relatively small number of particles (as used in this study), a time-averaging technique was used to determine the electric field. Based on the fact that RF plasma is a periodic phenomena, new electric field for a given time phase at the end of the n^{th} cycle is calculated using averaged density data of the previous $n/2$ cycles at the same time phase. In addition weighting factors were used to represent the charged particles and the neutrals. Further details can be found in Nagayama et al.¹².

Calculation conditions for the CH₄/H₂ plasma

The discharge is powered by RF source at 13.56 MHz. Eighty uniformly distributed grid points were used for the distance (2.5 cm) between the electrodes. 1,200 particles of each type are used. The gas is supplied from one electrode (anode). CH₄ and the neutral radicals produced by the reaction are partially eliminated under the condition that total pressure inside the chamber is held constant. The secondary electron emission coefficient was set to zero for all calculations reported here. In surface reactions, C-H or C₂-H is absorbed to form film and hydrogen is released. Accordingly, the depositing particles are eliminated from the calculation and hydrogen particles are added. Anisotropic angular scattering is incorporated with the relative differential cross section for all electron and neutral collisions. Electron wall reflection ratio is set to 0.25. The calculations are carried out for 1200 RF cycles and the data are averaged between 600th - 1200th cycles for calculating the plasma properties. Time steps considered were between 0.001 and 1.0 ns for a charged particle depending on its velocity. Larger time steps were considered for the neutrals¹².

For all calculations, the driving voltage (V_{RF}) is set to 200 V, and the DC bias voltage (V_{DC}) is equal to zero. Flow rate and gas compositions or pressure were changed. Two cases of simulations were carried out.

Case 1: Total flow rate is fixed to 24 sccm, and supply gas composition CH₄/(CH₄ + H₂) ratio is varied keeping the total pressure at 400 mTorr.

Case 2: CH_4 flow rate is fixed to 24 sccm, and H_2 flow rate is changed keeping the CH_4 partial pressure to 100 mTorr.

RESULTS AND DISCUSSION

Case 1: Fixed total flow rate with varying composition

Simulations were carried out at different H_2 partial pressures (300, 200, and 0 mTorr), while total pressure is kept constant (400 mTorr). In other words, the gas composition is changed while total pressure is kept constant. The simulated power consumption and current in the plasma (as a function of the gas composition) are shown in Fig. 1-a.

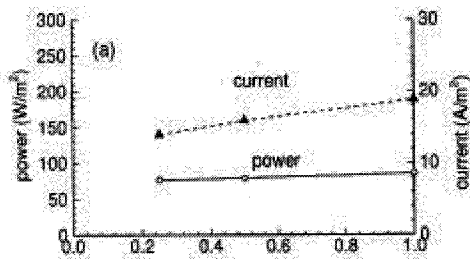


Figure 1-a. Power and displacement current as function of $\text{CH}_4/(\text{CH}_4 + \text{H}_2)$

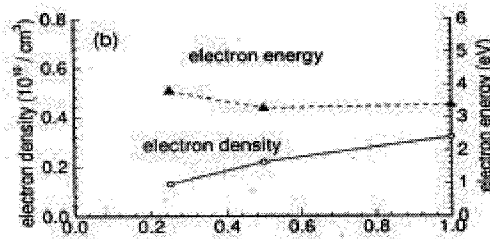


Figure 1-b. Electron energy and electron density (at the center of the discharge) as function of $\text{CH}_4/(\text{CH}_4 + \text{H}_2)$

Note that small values of $\text{CH}_4/(\text{CH}_4 + \text{H}_2)$ value indicates that the gas composition is highly diluted by hydrogen. Power consumed in the reactor does not depend on the gas composition in the simulated range. Total current tends to increase as CH_4 ratio increases, which may be related to the increase of plasma density. Fig. 1-b shows the electron density and electron energy values at the center of the discharge as a function of the above ratio.

Electron density increases as CH_4 ratio increases because the CH_4 ionization is the major source of electrons. Electron energy is between 3.4 - 3.8 eV in the simulated range. The electron-impact ionization and dissociation rates are shown in Fig. 1-c as function of the inlet gas composition ratio.

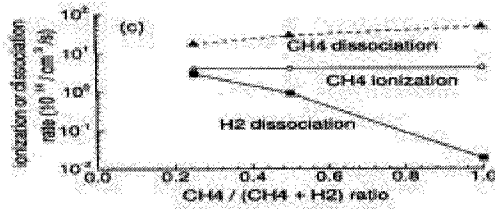


Figure 1-c. Computed (electron-impact) reaction rates as a function of $CH_4/(CH_4 + H_2)$

CH_4 dissociation rate is about ten times higher than CH_4 ionization rate and the variations are small in the log scale. Although H_2 dissociation rate is negligible in pure CH_4 plasma, H_2 dissociation rises to the same level as CH_4 ionization rate at highly diluted condition. Although we neglected H_2 ionization process in this model, the assumption is reasonable because such rate will be lower than H_2 dissociation and will be negligible compared to CH_4 ionization and dissociation in the simulated range.

Fig. 2 shows the radical and neutral densities as functions of the $CH_4/(CH_4 + H_2)$ ratio. CH_4 increases and H_2 decreases as the gas composition is changed. H density does not change much although H_2 density increases significantly. The reason may be that H is generated from both CH_4 and H_2 dissociation. CH_3 density

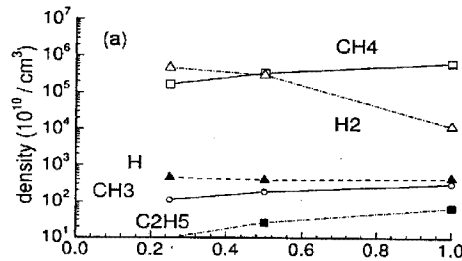


Figure 2. Computed neutral density profiles as functions of $CH_4/(CH_4 + H_2)$

increases as and CH_4 dissociation increases. C_2H_5 density also increases as CH_3 density increases.

The energy of ions impinging to the cathode tends to decrease as CH_4 density increases and charge exchange collisions increase. It is noted that the present model does not consider the interaction between CH_4 ion and H_2 . Fig. 3 shows the deposition rates for the three depositing species as function of the $CH_4/(CH_4 + H_2)$ ratio. CH_3 and C_2H_5 deposition rates increase as CH_4 density increases. C_2H_5 represents PAHs (polyatomic hydrocarbon) and high C_2H_5 may cause polymer like films. On the other hand CH_4^+ deposition rate is constant because ionization rate does not change.

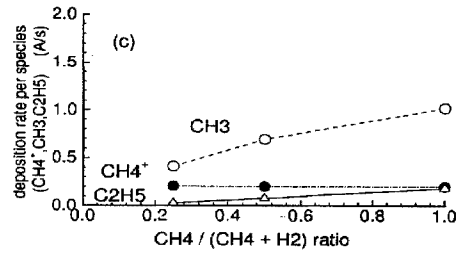


Figure 3. Deposition rates as function of functions of $\text{CH}_4/(\text{CH}_4 + \text{H}_2)$

Case 2: CH_4 flow rate is fixed while hydrogen is added

Simulations were also carried out at different H_2 flow rates (0, 48, 96 sccm), while CH_4 flow rate is kept constant at 24 sccm. The CH_4 partial pressure is thus indirectly fixed at 100 mTorr. The power consumption and current are high for high H_2 addition. It means power is mostly consumed by electron-hydrogen collision. Although H_2 density increases as the dilution becomes high, the density levels of most species do not change as in the previous case. The ion energy is between 24 - 28 eV and does not show any variation with hydrogen addition. As noted before, no interactions between CH_4^+ and H_2 , were considered here.

Fig. 4 shows the spatial profiles of time averaged rate coefficients for different values of H_2 pressure as CH_4 pressure is held constant at 100 mTorr.

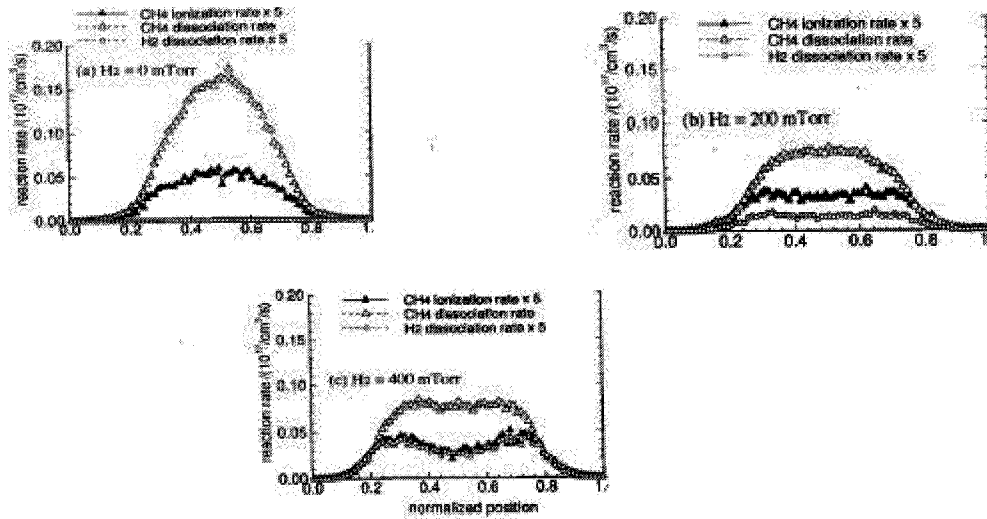


Figure 4. Time averaged rate coefficient profiles for electron-impact reactions with varying H_2 addition

With pure CH_4 , dissociation rate is large and H_2 dissociation is negligible (Fig. 4-a). The CH_4 dissociation rate is high at the center of the plasma that is typical at low pressure (100 mTorr). As the H_2 pressure is increased (Fig. 4-b, c), H_2 dissociation is increased. It is interesting to note that by adding H_2 the spatial profile of the rate coefficients become bow

shaped, which is similar to the case of pure gas discharges where pressure is increased. At H₂ pressure of 400 mTorr (80% of the total flow), H₂ dissociation rate is comparable to CH₄ ionization rate but still about ten times smaller than CH₄ dissociation rate. H₂ dissociation and CH₄ ionization rates are high in the sheath region while CH₄ dissociation rate is uniform in the plasma bulk at this pressure (Fig. 4-c). The reason may be due to the fact that in the former two processes, high energy (threshold energy is 13 eV for H₂ dissociation and 14 eV for CH₄ ionization) is needed compared to CH₄ dissociation (threshold energy is 10 eV).

CONCLUSIONS

Particle-in-cell/Monte Carlo simulations of capacitively coupled RF (radio-frequency) glow discharges were carried out for low pressure CH₄/H₂ plasmas. The model employs a one-dimensional scheme and considers polyatomic particle motion and collision. Calculations were carried out for two cases: (a) total flow rate is fixed while gas composition or CH₄/(CH₄ + H₂) ratio is varied, and (b) CH₄ flow rate is fixed while H₂ flow rate is changed. When CH₄ flow rate is decreased, the gas density in the chamber and deposition rate decrease significantly for carbon containing radicals while CH₄⁺ density does not change much. On the other hand, when CH₄ flow rate is fixed and H₂ flow rate is increased, and deposition rate decrease similarly, but the gas density in the chamber does not change much (for the range of parameters considered). For both cases, H₂ dissociation rate is comparable to CH₄ ionization rate when H₂ partial pressure is about 75 ~ 80% of the total gas pressure. However, H₂ dissociation rate is still very small compared to CH₄ dissociation rate. When H₂ flow rate increases with fixed CH₄ flow rate, lower CH₃ and C₂H₅ deposition rates occur, but the overall effect is not large (H₂ flow rates between 0 to 80% of the total flow). The major reason is that electron impact dissociation cross section of hydrogen is smaller than that of CH₄. With the addition of H₂, carbon-containing gas decreases significantly and deposition rate is decreased especially for C₂H₅ while that for CH₄⁺ does not change much. This may improve the film quality suppressing the PAHs formation. Adding H₂ also changes the rate coefficient spatial profiles to bow shape, which is similar to the case of pure gas discharges when pressure is increased.

REFERENCES

1. K. E. Spear and J. P. Dismukes, *Synthetic Diamond: Emerging CVD Science and technology*. John Wiley & Sons, Inc. (1994)
2. M. Frenklach, *J. Appl. Phys.* **65** (12), 5142 (1989)
3. Y. Catherine and P. Coudrec, *Thin Solid Films* **144**, 165 (1986)
4. L. E. Kline, W. D. Partlow, and W. E. Biee, *J. Appl. Phys.* **65** (1), 70 (1989)
5. A. Rhallabi and Y. Catherine, *IEEE Trans. Plasma Sci.* **19** (2), 270 (1991)
6. E. Gogolides, D. Mary, A. Rhallabi, G. Turban, *Jpn. J. Appl. Phys.* **34** 261 (1995)
7. A. von Keudell and W. Moller, *J. Appl. Phys.* **75** (12), 7718 (1994)
8. K. Tachibana, M. Nishida, H. Harima, Y. Urano, *J. Phys. D: Appl. Phys.*, **17**, 1727 (1984)
9. E. Gogolides, D. Mary, A. Rhallabi, G. Turban, *Jpn. J. Appl. Phys.* **34** 261 (1995)
10. T. J. Sommerer and M. J. Kushner, *J. Appl. Phys.* **71** 1654 (1992)
11. N. Sato and H. Tagashira, *IEEE Tran. Plasma Sci.* **19** 102 (1991)
12. K. Nagayama, B. Farouk and Y.H. Lee, *IEEE Tran. Plasma Sci.* **26** (2), 125 (1998)
13. G. A. Bird, *Molecular Gas Dynamics and The Direct Simulation of Gas Flow*, Oxford University Press, New York, NY, 1994
14. C. Borgnakke and P. S. Larsen, *J. Comp. Phys.* **18**, 405, (1975)
15. D. J. Economou, T. J. Bartel, R. S. Wise and D. P. Lymberopoulos, *IEEE Trans. Plasma Sci.* **23**, 581 (1995)
16. W. L. Morgan, *Plasma Chem. Plasma Process.*, **12** (4), 477, (1992)