Theoretical study to investigate the impact of plasma parameters on the catalyst nanoparticle growth

To cite this article: R Gupta et al 2017 J. Phys.: Conf. Ser. 836 012024

View the article online for updates and enhancements.

Related content
- Control of growth mode of multiwalled carbon nanotubes
  Nguyen Hong Quang and Do-Hyung Kim
- Kinetic Calculations in Plasmas Used for Diamond Deposition
  Pierre Bou, Jean Claude Boettner and Lionel VandenBulcke
- Carbon saturation of arrays of Ni catalyst nanoparticles of different size and pattern uniformity on a silicon substrate
  I Levchenko and K Ostrikov
Theoretical study to investigate the impact of plasma parameters on the catalyst nanoparticle growth

R Gupta*, S C Sharma and N Gupta
Department of Applied Physics, Delhi Technological University, Delhi-110042, India
Email: *ravigpt0709@gmail.com

Abstract. The plasma kinetics based model is adopted to elucidate the effect of plasma parameters on the nucleation and growth mechanism of catalyst nanoparticle. The present model considers the plasma processing of thin catalyst film, power equalization at the film surface, flux and kinetics of plasma species (electrons, ions, and neutrals). In our investigation, it is found that catalyst nanoparticle diameter decreases with increase in ion number density in plasma. Moreover, it is also found that catalyst film thickness significantly affect the catalyst nanoparticle size i.e., catalyst nanoparticle diameter increases with catalyst film thickness. In addition, it is observed that the substrate temperature increases during the plasma processing and finally achieve saturation. Our theoretical results are in good agreement with the experimental results.

1. Introduction
The catalyst nanoparticles are the fundamental site for the nucleation of nanostructures and significantly influence the structure, shape and size of the nanostructure [1]. These catalyst nanoparticles can be synthesized using the plasma technique, i.e., plasma sputtering and etching of the thin film[2]or by thermal annealing of the thin film deposited on substrate surface. During the plasma treatment of thin film, plasma parameters extensively affect the catalyst nanoparticle span (diameter). Chang et al. [3] experimentally observed that the catalyst nanoparticle size obtaining from thin catalyst film decreases with increases in plasma power.

So far only thermodynamics based theoretical models are available to depict the size of the catalyst nanoparticle obtained from the thin catalyst film. In the present paper, in section 2, we have devised the plasma based model to elucidate the growth mechanism of catalyst nanoparticle resulting from the etching and sputtering of the thin film in the reactive plasma, i.e. plasma treatment of the thin catalyst film. The results of the model are discussed in the section 3 and finally conclusion is given in section 4.

2. Model
The model acknowledges the kinetics and energy fluxes of various plasma species (electrons, positively charged ions and neutrals), power equalization at the catalyst film-substrate surface, and heat radiations. The present model accounts the reactive plasma consisting electrons, ions and neutrals of hydrogen. It is assumed that, the spherical catalyst nanoparticles are formed as a result of sputtering and etching of the catalyst film during the plasma treatment.
2.1. Kinetic equation of electrons, positively charged ions, and neutrals in the reactive plasma

\[ \dot{n}_e = \beta n_i - \alpha n_e n_i - \gamma e n_a \eta_{ef} \]  
\[ \dot{n}_i = \beta n_i - \alpha n_e n_i - n_a J_{lcf} - J_{ad} + J_{desp} \]  
\[ \dot{n}_1 = \alpha s n_e n_1 - \beta n_1 + n_a (1 - \gamma_1) j_{l1} - n_2 \gamma_1 j_1 \]

where subscript 1 denotes the hydrogen, \( \beta \) is the coefficient of ionization of the constituent neutral atoms due to external field, \( n_2 \) is the number density of neutral atom, \( n_e \) is the electron number density, \( n_i \) is the ion number density, \( \alpha_i(T) = \alpha_i(300/T_e)^k \) cm\(^3\)/sec is the coefficient of recombination of electrons and positively charged ions, \( k = -1.2 \) is a constant, \( \eta_a \) is the number of catalyst particle per unit area \( \gamma_i \) is the ion sticking coefficient, \( \gamma_2 \) is the sticking coefficient of neutral atoms \( J_{ad} \) is the adsorption flux onto the catalyst substrate surface, \( J_{desp} \) is the desorption flux from the catalyst-substrate surface, \( j_{lcf} \), \( j_{lacf} \) and \( j_{af} \) are the collection currents on the film surface due to electrons, ions and neutrals, respectively [4].

Equations (1), (2), and (3) indicate the balance of electrons, ions, and neutral atoms number density in the reactive plasma. The first of equation (1) denotes the gain in electron density per unit time due to ionization of neutral atoms; second and third terms refer to the decay rate due to electron-ion recombination and electron collection current at the film surface, respectively.

The first term of equation (2) describes the gain in ion number density due to ionization of neutral atoms. The second and the third terms represent the decay rate of positively charged ion density due to electron-ion recombination and ion collection current at the surface of the film, respectively. The fourth and fifth terms indicate adsorption and desorption of ions to/from the film surface, respectively.

The First and third terms of equation (3) show the growth rate of neutral density due to electron-ion recombination and neutralization of ions collected at the film surface, respectively. The second and fourth terms represent the decay rate of neutral density due to ionization and accumulation of neutrals on the film surface, respectively.

2.2. The power equalization at the catalyst film surface

\[ \dot{H}_{input} = H_g + H_{output} \]  
\[ \dot{H}_g = \frac{d}{dt} \left( m_{cf} \hat{S}_f \tilde{\theta}_S \right) = A_{cf} \Sigma_{cf} \left( \tau_{cf} \frac{d \tilde{\theta}_S}{dt} + \eta_a \theta_a \frac{d}{dt} \left( \frac{1}{6} \pi d^3 \right) \right) \]  
\[ \dot{H}_{output} = \Lambda_{cf} (1 - \kappa_c) \left( \hat{S}_S - \frac{3}{2} k_B \frac{\theta_a}{\tilde{\theta}_S} \right) \right) \]  

where \( A_{cf} \) is the catalyst film surface area, \( \tau_{cf} \) is the catalyst film thickness, \( d \) is the catalyst nanoparticle diameter (it is assumed that catalyst nanoparticle of spherical morphology are formed as result of plasma treatment of thin catalyst film), \( \theta_a \) is the substrate temperature (in the present model temperature of substrate and thin catalyst film is assumed to be same), \( \theta_j \) is the mass of catalyst film,
\( \kappa_{il} \) and \( \kappa_{l} \) are the ion sticking coefficient and neutral atom sticking coefficient, respectively, \( s_f \) is the specific heat of the film, \( \varepsilon_{rrn} \) is the emissivity of the surrounding, \( \varepsilon_{cf} \) is the emissivity of the film, \( \varepsilon_{ef} \), \( \varepsilon_{il} \), and \( \varepsilon_{if} \) are the mean energy of electrons, ions and neutrals, respectively, collected by film [6]. \( \Lambda_{ef} \) is the energy loss during collision with film, \( \nu_0 \) is the no. of sites available, \( \sigma_{ads} \) is the cross-section area, \( \phi_a \) and \( \phi_{ia} \) are neutral and ion fluxes, respectively, \( E_B \) is the binding energy of the material, \( \sigma \) is the Stefan's constant and \( \Theta \) is the total surface coverage.

The first term in equation (5) represents the power given to the film surface by the electrons, ions and neutral atoms, the second term denotes power towards the film surface due to heat radiations from surrounding, and the third term is power collected by film surface due to formation of neutrals at the film surface. The equation (6) describes the power gained during the plasma treatment of thin catalyst film. The input plasma power causes the thin catalyst film into nanoparticles and also causes the increase in substrate temperature. The equation (7) describes the power loss due to sticking and elastic collision of electrons with catalyst film surface, power output from the surface to the surrounding in the form of radiations, power loss in etching and sputtering of thin film in the presence of plasma, respectively.

3. Results and discussion

The model acknowledges the different physical process responsible for the formation of catalyst nanoparticle from thin catalyst film in the presence of plasma and hence the model relates the diameter of the catalyst nanoparticle formed with the plasma parameters such that number density of the electrons, ions, and neutrals, plasma power, and thin film thickness.

The figure 1 shows the time evolution of catalyst nanoparticle diameter for various thin film thickness. From figure 1, it can be seen that diameter of the catalyst nanoparticle increases with thickness of the thin film.

The figure 2 shows variation of catalyst nanoparticle diameter with plasma power. As plasma power increases the catalyst nanoparticle diameter decreases. This is attributed to the fact that with increase in plasma power highly energetic plasma species (electrons, ions, and neutrals) are created in the reactive plasma that leads to higher etching and sputtering of the catalyst thin film resulting in the lesser catalyst nanoparticle diameter.

The figure 3 shows the variation of substrate temperature during the plasma treatment of the thin catalyst film. The substrate temperature increases during the plasma treatment and achieves the saturation after sometime. The highly energetic plasma species transfer their energy to the film surface during the bombardment and collisional processes with the film surface and thus increase the film surface/substrate temperature. These theoretical findings are in good agreement of the experimental observations of Poa et al. [7], Chang et al. [3], and Srivastava et al. [8].

![Figure 1](image1.png)  
**Figure 1.** The time evolution of catalyst nanoparticle diameter for various catalyst film thicknesses.

![Figure 2](image2.png)  
**Figure 2.** The time evolution of catalyst nanoparticle for different input plasmapower.
Figure 3. The time variation of substrate temperature during the plasma processing (plasma treatment) of the thin catalyst film in the plasma containing electrons and ions and neutrals of hydrogen.

4. Conclusions
An analytical model to relate the catalyst nanoparticle diameter with plasma parameters (number density of plasma species, their temperatures, and plasma power) and catalyst film thickness during the plasma treatment catalyst film has been developed. It is found that diameter of spherical catalyst nanoparticles increases with catalyst thin film thickness and decreases with plasma power. Moreover, we found that substrate temperature also increases during the plasma treatment of thin film and after some time achieves the saturation. The present work could foresee the catalytic synthesis of the carbon nanostructure in near future.

References
[1] Yang R T and Chen J P 1989 J. Catal 115 52
[2] Yudasaka M, Kikuchi R, Matsui T, Ohki Y, Yoshimura S and Ota E 1995 Appl. Phys. Lett. 67 2477
[3] Chang S C, Lin T C and Pai C Y 2007 Microelectron. J. 38 657
[4] Shrama S C and Gupta N 2015 Phys. Plasmas 22 123517
[5] Kersten H, Deustch H, Steffen H, Kroesen G M W and Hippler R 2001 Vacuum 63 385
[6] Sodha M S and Guha S 1971 Physics of Colloidal Plasmas (New York: John Wiley & Sons) p 219
[7] Poa C H P, Henley S J, Chen G Y, Adikaari A A D T, Giusca C E and Silva S R P 2005 J. Appl. Phys. 97 114308
[8] Srivastava S K, Shukla A K, Vankar V D and Kumar V 2005 Thin Solid Films 492 124