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MODEL FOR DEPOSITION OF THIN FILMS IN PLASMA CVD

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Abstract

A simplified model is proposed to describe the deposition process of thin films in plasma CVD techniques. The film deposition rate is explained by the terms of fluxes of reactive species and fluxes of particles etched from the substrate and diffused into bulk substrate. Several examples of the film deposition are discussed, based upon the present particle balance equation. The particle balance in the ion beam implantation technique is also briefly discussed.

1. Introduction

In the field of thin film coatings and surface modifications, numerous low temperature techniques called as plasma CVD and ion beam techniques have been widely used1)-6). The advantage in use of low temperature plasma for coatings is high deposition rate of film due to a large quantity of reactive species1). On the other hand, the ion beam technique enables us to precisely control the surface properties, e.g. implantation depth and quantity. In both techniques, however, the film growth rate or the density balance of the implanted particles has not been analytically discussed in detail yet. One possible reason is due to the complexities of both plasma state, and particle deposition or implantation process.

In the plasma CVD, the film deposition depends on the impinging reactive species and fluxes, and the interactions with the surface such as particle migration and the sticking probability. During the deposition process, the deposited atoms or particles may be lost by the etching due to impinging particles and the diffusion into the bulk substrate. While the data on the film deposition process have not been obtained yet, it may be possible to consider the particle balance for the thin film deposition. In the present note, the particle balance for the deposition of a thin film in the plasma CVD is suggested, and then the deposition rate is evaluated for several examples in the plasma CVD such as the carbonization experiment. In addition, the particle balance of the surface layer in the ion beam implantation technique is also briefly discussed.

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2. Particle Balance for Deposition of Thin Film in Plasma CVD

The deposition of a thin film is due to the reactive species in the plasma such as ions, radicals, metastables, excited neutrals, atoms and dissociated molecules. These species are physically or chemical absorbed on surface. Since the physical bonding energy is generally much less than that of chemical bonding, the chemical adsorption is required for the film growth. The sticking probability of the reactive species is a function of numerous parameters, e.g. ability of particles to form chemical bondings, substrate temperature and surface roughness. The crystal structure of film also depends on the particle migration determined by the surface state such as the substrate temperature and the surface roughness, and the deposition flux. In general, the crystal structure with thermodynamically stability is obtained when the particle migration is enhanced, e.g. in a case with high substrate temperature and low deposition flux.

The deposited film, on the other hand, is etched by the processes of evaporation, physical sputtering and chemical sputtering. In addition, the deposited atoms may be lost into the bulk substrate through the diffusion when the substrate temperature is quite high. The segregation of the element of the bulk into the film may occur if the ability to form the chemical compound with the film atom is considerably large.

Based on the above arguments, we may be able to illustrate the film deposition process as shown in the Fig.1. In this figure, the crystality and the segregation of bulk element are not taken into account. According to the figure, we now consider the particle balance to estimate the film deposition rate. The deposition flux of reactive species, Φ_d, is written by

$$\Phi_d = \sum_i \eta_s^i \Phi_r^i \qquad \text{——(1)}$$

where η_s^i is the sticking probability of reactive species i and Φ_r^i the flux of reactive species i. The flux of etched particles is expressed as

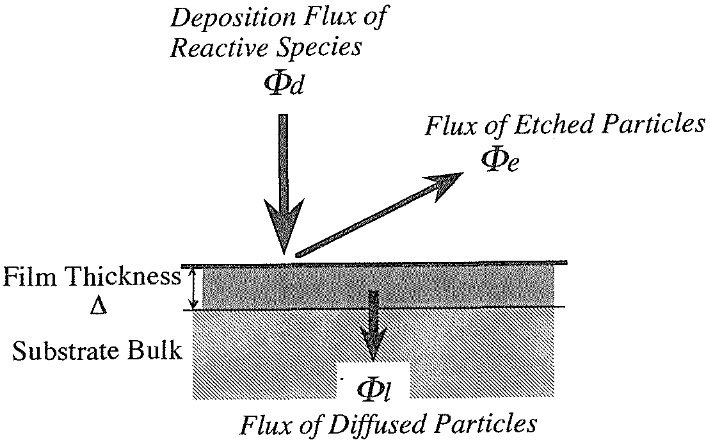

Fig. 1 Model for deposition of thin film.

$$\Phi_e = \Phi_{eva} + \sum_i (Y_p^i + Y_c^i)\Phi_r^i \qquad (2)$$

where Φ_{eva} is the evaporated/sublimated flux, and Y_p^i and Y_c^i are the physical and the chemical sputtering/erosion yields due to reactive species, respectively. As the examples of the chemical sputtering, the following reactions are cited:

$$\begin{cases} O+C \rightarrow CO \text{ (Graphite Erosion by Oxidation)} \\ 4H+C \rightarrow CH_4 \text{ (Graphite Erosion by Formation of Hydrocarbon)} \\ 4H+Si \rightarrow SiH_4 \text{ (Silicon Erosion)} \end{cases}$$

The flux of the particle diffusion from the film to the bulk substrate is given by

$$\Phi_l = n v_p \qquad (3)$$

Here, n is the atom density of film. The atom density is related with the mass density, ρ, the thickness of monolayer, l, mass of film atom, m_i, and the monolayer density per unit area, n_m, in the followings:

$$n = \frac{n_m}{l} = \frac{\rho}{m_i} \qquad (4)$$

The diffusion velocity, v_p, is approximated as

$$v_p \simeq \frac{D_o e^{-\frac{E_a}{kT_{sub}}}}{\Delta} \qquad (5)$$

where D_o is the diffusion constant, E_a the activation energy, T_{sub} the substrate temperature and $k=8.61\times10^{-5}$ (eV/K) the Boltzmann constant.

The particle balance equation, from Eqs. (1), (2) and (3), becomes

$$\left(\frac{\rho}{m_i}\right)\frac{d\Delta}{dt} = \Phi_d - \Phi_e - \Phi_l$$

$$\simeq \sum_i \eta_s^i \Phi_r^i - \left(\Phi_{eva} + \sum_i (Y_p^i + Y_c^i)\right) - \frac{D_o e^{-\frac{E_a}{kT_{sub}}}}{\Delta} \qquad (6)$$

where Δ is the film thickness. In Eq.(6), $d\Delta/dt$ expresses the film deposition rate.

3. Simplified Cases and Examples

We first consider the carbon film deposition by using a DC glow discharge for the mixture gas of CH_4 and $H_2$7)-12). It is assumed that the substrate temperature is low enough for both the diffusion and chemical sputtering be ignored, and the energy of the ion is low, e.g. no physical sputtering. It is known that the hydrocarbon ions such as CH_4^+ may be very effective for the film deposition. In this case, Eq. (6) is written by

$$\left(\frac{\rho}{m_i}\right)\frac{d\Delta}{dt} \sim \eta_s \Phi_{CH_x} \qquad (7)$$

where Φ_{CH_x} is the flux of hydrocarbon ions. Assuming that $\rho=1.5$ g/cm³, $m_i=2.7\times10^{-23}$ g, $\eta_s=1$, the total beam current density $j=10$ μA/cm² and the beam density of hydrocarbon ions is $j/10$, we obtain the deposition rate of the carbon film as $d\Delta/dt=10$ Å/min. The estimated value is close to the experimental value in the carbonization of a fusion device such as Heliotron E[12)].

In the case of deposition of diamond like film due to the plasma CVD[8)], the effect of the etching is relatively important. The density balance equation may be written as

$$\left(\frac{\rho}{m_i}\right)\frac{d\Delta}{dt} \sim \eta_s\, \Phi_{CH_x} - Y_c\, \Phi_H \qquad \text{——(8)}$$

where Φ_H is the flux of reactive hydrogens. In the preparation of diamond like film due to the plasma CVD, the ratio of hydrocarbon gas such as CH_4 to hydrogen gas H_2 is about 1%. In addition, the diffusion of carbon atoms can be ignored if the substrate temperature T_{sub} is much less than 1000 °C.

Assuming that $\eta_s=1$, $Y_c=0.01$, $\rho=2$ g/cm^3, $\Phi_{CH_x}=1.3\times10^{14}$/cm^{2}s and $\Phi_H=5.3\times10^{15}$/cm^2 s, we have the deposition rate, $d\Delta/dt=3$ Å/min. Compared with the case of the carbon film deposition, the deposition rate becomes several times lower since the etching flux is relatively large. The present estimation can not give the precise deposition rate, because of the lacking of the data on the parameters such as Φ_{CHx}, Φ_H and Y_c. However, the present model can explain the parameter dependency on the deposition of the diamond like film in the plasma CVD.

When only the etching term is dominant, the density balance can be given by

$$-\left(\frac{\rho}{m_i}\right)\frac{d\Delta}{dt} \sim (Y_p+Y_c)\Phi_r \qquad \text{——(9)}$$

As the example, considered is the chemical erosion of the carbon film or the graphite due to hydrogen ions[13)]. When the substrate temperature is about 500 °C, Y_c becomes ~ 0.1. The etching rate, $-d\Delta/dt$, in this case, becomes $\sim$ 50 Å/min when the current density of hydrogen ions is 1 mA/cm^2.

The diffusion term should become to be dominated when $D_o\, exp(-E_a/kT_{sub})/\Delta \simeq d\Delta/dt$. In the case that $D_o \sim 10^{-12}$ cm^2/s, $\Delta \sim l \sim$ Å, and $E_a=1$ eV, the particle loss rate $-d\Delta/dt$ becomes of order of Å/s when $T_{sub}\sim 1000$ °C. In this case, thus, it can be regarded that the diffusion term should be taken into account when the substrate temperature becomes close to roughly 1000 °C.

4. Density Balance for Ion Beam Implantation Process

In the case of implantation of high energy ions[14)], the sputtering of bulk substrate may be ignored because of the deep penetration. Figure 2 shows the illustration for density balance of implanted particles. The implantation depth may be determined by the energy loss per unit length, dE/dx. There may be an upper limit of accumulated density in the depth up to the range, If no diffusion of implanted particles into the bulk substrate occurs, the injected beam particles may be reflected or self-sputtered, or easily penetrate into the depth region deeper than the range.

The density balance from the top surface to the range, before the density saturation, can be describe by the equation

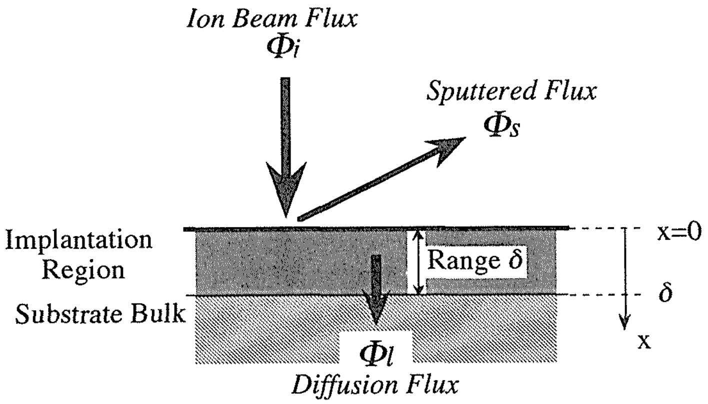

Fig. 2 Model for particle balance of ion implantation.

$$\frac{dn}{dt} \simeq \frac{nv_p}{\delta} + S(x) \qquad \text{——(10)}$$

where v_p is the velocity of diffusion into the bulk substrate, δ the range, and $S(x)$ the implantation rate per unit volume. $S(x)$ is approximated as

$$S(x) \simeq \frac{\Phi_i}{\delta} \qquad \text{——(11)}$$

Here Φ_i is the flux of ion beam.

As the example, we consider the implantation of hydrogen ions into the graphite. The maximum hydrogen ratio to carbon atom is known as H/C=0.4 at RT. When the graphite density is 2 g/cm^3, the beam current of hydrogen ions is 0.1 mA/cm^2 and the range of hydrogen ions (energy=1keV) is 200 Å, the hydrogen level be saturated after the irradiation of 140 seconds. After the density saturation, the injected particles may be reflected or self-sputtered, or quickly diffuse into the bulk region. If the diffusion flux, nv_p, becomes larger compared with the beam flux, the implantation continuously occurs, and the implanted depth be expanded.

5. Summary

The deposition rate of the thin films in plasma CVD techniques is analytically expressed in terms of the deposition flux, the etched flux and the diffusion flux. As the examples, the deposition rates of the carbon film and the diamond like film are evaluated. The obtained values well express the tendency of the experimental values while the data on the fluxes of reactive species are not well aviable.

The density balance of implanted particles in ion beam implantation technique is also briefly discussed.

The present model both for the thin film deposition and the implanted density may be useful to understand the film growth process and the ion beam implantation process.

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