CHAPTER 3

Ion Sputtering of Biological Organism

The sputtering depends on many factors, such as the energy of the incident ion, ion dose, ion species, target material and incident angle. The heavier the ion the greater the yield and the higher the energy at which the sputtering yield levels off.

The requirements of molecular analysis in biological organisms are very demanding. When a primary ion beam with a certain energy, mass, and charge state bombards a solid target, interaction between ions and target would base on an accurate description of the bullet-target analogy. But the studies of the interaction between energetic ions and the living biological target are much more complicated.

Biological organism is composed of solid, fluid and gas which lead to less stability than solid material. The biological structure is separated into many cells, and a cell is further divided into many smaller compartments yielding further complication.

The sputtering yield *Y* depends on the surface binding energy and the mass density or atomic density of the target material. For compounds or mixtures, the different atomic species have different partial sputtering yields. This partial yield is proportional to the species surface concentration. For the case of the cellulose compounds such as the primary constituent of plant cell walls, if the partial yields of C, H and O can be obtained, the average total yield can be taken to be the sum of the three partial yields. In order to estimate the partial yields and the surface binding.

In this chapter (Yu, No date), the erosion of biological organisms by ion sputtering and electron sputtering is described. This actually provides subsequent incident ions with passages in which the ions have no energy loss. The target atom volume density along the ion implantation direction after implantation to a certain dose can be expressed as

$$N(x) = \begin{cases} 0 \text{ at vacancies } (-l, \alpha l), \\ \qquad\qquad\qquad\qquad\qquad \text{(for } \alpha\text{, see below)} \\ N \text{ at non-vacancies } (\alpha l, l). \end{cases} \qquad (3.1)$$

In the interval (*-l*, *l*), expansion of the above expression as a Fourier series gives

$$N(x) = a_0 / 2 + \sum_{n=1}^{\infty} (a_n \cos n\pi x / l + b_n \sin n\pi x / l) \qquad (3.2)$$

where

$$a_0 = N(1 - \alpha)$$

$$a_n = -\frac{N}{n\pi} \sin n\pi\alpha,$$

$$b_n = \frac{N}{n\pi} [\cos n\pi\alpha - (-1)^n].$$

With these expressions, Equation (3.1) becomes

$$N(x) = \frac{(1-\alpha)}{2} N + \sum_{n=1}^{\infty} \frac{N}{n\pi} \{[(\cos n\alpha\pi) - (-1)^n] \sin n\pi x / l - \sin n\alpha\pi \bullet \cos n\pi x / l\} \qquad (3.3)$$

In the above expression, (*-l*, *l*) is the distribution period of the atomic density of the biological organism in the direction of the ion trajectory. It should be pointed out that this biological material density distribution is not a periodic function. As for the initial implantation dose, the distribution of the vacancies and biological channels formed in the direction of the ion trajectory is statistical. If the ions do not lose their energy when they are traveling in the vacancies (provided that the geometrical dimension of the vacancies is much greater than the ion radius so that the interaction between the moving ions and the vacancy walls can be neglected), then only vacancies along the ion trajectory are considered, no matter where in the trajectory they are.

The parameter α is dimensionless, indicating the fraction of vacancies along the trajectory, and its value is determined by Equation (3.1) between *–l* and *l*. The value of α is closely related to the biological organism (such as the dry crop seed) structure, implanted ion dose, sputtering coefficient, and so on. In the process of ion

implantation, as the implanted ion dose increases the dimension of the vacancies in the biological organism may increase and new combined vacancies may also be produced, as has been experimentally observed. The ion beam acts like a milling cutter, eventually possibly linking vacancies in the region near the surface of the organism. This provides subsequent ions with a section of unimpeded passage, which, for example as in the gene transfer process, can allow plasmid DNA that is greater than the implanted ion radius to pass through smoothly.

Based on the above analysis, the physical meaning of α can be given. If N is the atomic volume density (not including vacancies) of the biological organism and A is the ion implantation area, the number of total target atoms in a distance $2l$ along the implantation direction is $N{\cdot}A{\cdot}2l$. If these atoms are moved to area A, the target area density is then

$$N_A = 2l{\cdot}N. \tag{3.4}$$

In the above volume, the vacancy volume intrinsically in the organism is specified as η. If the atoms that can be contained in these vacancies are moved to area A, the number of vacant atoms per unit area is then

$$N_C = 2\eta l{\cdot}N. \tag{3.5}$$

Now the effects of ion and electron sputtering and chemical sputtering are taken into account. The number of the target atoms emitted per unit area is

$$N_S = \mathrm{rD}, \tag{3.6}$$

where D is the implantation dose, and r is a coefficient related to the particle emission. Hence the total number of lost target atoms per unit area in terms of distance in the ion incident direction is

$$l' = \frac{N_S + N_C}{N} = \frac{rD}{N} + 2\eta l\ . \tag{3.7}$$

From Equation (3.1), l' is known as the section in $(-l, l)$ with zero density, namely,

$$l' = l + \alpha l, \quad \alpha = \frac{l'}{l} - 1.$$

Use of l and l' in Equation (3.4) and (3.7) in the above expression results in

$$\alpha = \frac{\frac{rD}{N} + 2\eta l}{\frac{N_A}{2N}} - 1 = \frac{2rD}{N_A} + \frac{2\eta \bullet 2Nl}{N_A} - 1.$$

Since

$$-\frac{dE_1}{dx} = \frac{(1-\alpha)}{2} + \sum_{n=1}^{\infty} \frac{N}{n\pi} \left\{ \left[\cos n\alpha\pi - (-1)^n \right] \sin n\pi x / l - \sin n\alpha\pi \bullet \cos n\pi x / l \right\}$$

and

$$2Nl = \mathrm{NA},$$

thus

$$\alpha = \frac{2rD}{N_A} + 2\eta - 1. \qquad (3.8)$$

Since $\eta << 1$, when $D = 0$, α is very close to –1; when rD is close to N_A, then $\alpha \to 1$. Equation (3.8) gives a physical meaning to α and relates it to the ion implantation dose and the free space fraction in the biological organism.

Substitution of Equation (3.3) into $-\frac{dE_1}{dx} = N\left[S_n(E_1) + S_e(E_1)\right]$ results in

$$-\frac{dE_1}{dx} = \left\{ \frac{(1-\alpha)}{2} + \sum_{n=1}^{\infty} \frac{N}{n\pi} \left\{ \left[\cos n\alpha\pi - (-1)^n \right] \sin n\pi x / l - \sin n\alpha\pi \bullet \cos n\pi x / l \right\} \right\}$$

$$\times [S_n(E_1) + S_e(E_1)]. \qquad (3.9)$$

It can be seen that fluctuation of the incident ion energy loss along the direction of the ion trajectory is a feature of beaded energy deposition.

For low energy ion implantation, electronic stopping can be neglected and the total stopping power can be replaced by S_n. Integration of Equation (3.9) gives

$$\int_0^x N(x)dx = -\int_E^0 dE_1 / S_n = E_1 / S_n^0.$$

The left hand side of the above expression can be evaluated by integrating Equation (3.3):

$$\frac{(1-\alpha)}{2}x + \sum_{n=1}^{\infty}\frac{l}{n^2\pi^2}\left\{\left[\cos n\alpha\pi - (-1)^n\right](1-\cos n\pi x/l) - \sin n\pi x \bullet \sin n\pi x/l\right\}$$

$$= E_1 / NS_n^0 \qquad (3.10)$$

Neglecting the higher-order terms in Equation (3.10) gives

$$X = \frac{1-\alpha}{2} E_1 / NS_n^0 .$$

Using the α value in the above expression results in

$$X = \frac{N_A}{(1-\eta)N_A - rD} \bullet \frac{E_1}{NS_n^0} . \qquad (3.11)$$

Equation (3.11) indicates the possible penetration depth in the target material at the moment after implantation of the initial ion dose.

For the case of an ion implanted organism, η in Equation (3.11) is considerable (e.g. for crop seeds, η > 10%), and more importantly, the sputtering yield (here described by the emission coefficient *r*) is much greater than for metals and semiconductors.

The sputtering yield of ions etching an organism can be measured experimentally. For example, lactamine ($C_3H_7O_2N$) is a very good bio-equivalent material which can be used for such an experiment. This material was formed into a film with thickness 1.1 mg/cm^2 in an oven at 40^{o}C. The film was then implanted with 30 keV N^+ ions and the mass loss of the film then measured as a function of implantation dose. The results are shown in Figure 3.1 [Han J.W. and Yu, Z.L.]. Details of the mass loss are not taken into account. The mass loss is used to represent the sputtering yield (it can be imagined that the sputtering yield is greater than the mass loss, because some of the sputtered heavier pieces may fall back onto the film and its substrate and then be measured). One can calculate from Figure 3.1 that the emission coefficient *r* is 290 lactamine-molecules/ion or 3.8 × 10^3 atoms/ion.

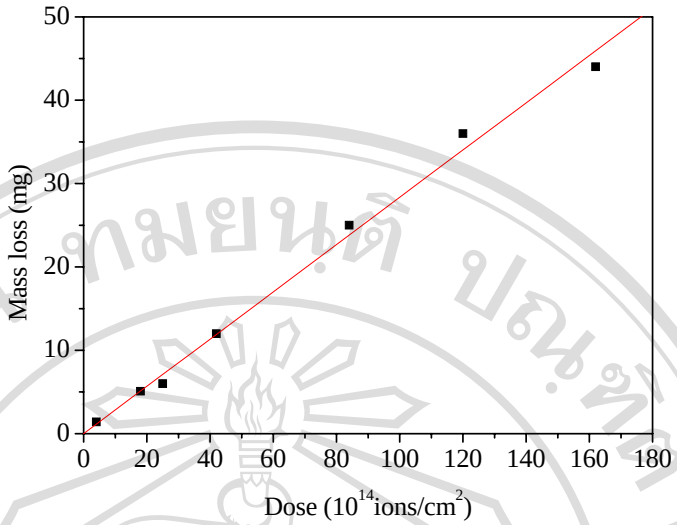

Figure 3.1. Mass loss of lactamine as a function of ion dose.

The biological cell contain a large quantity of water. Study the liquid (solid)-vapor two-phase equilibrium can describe how to study the sputtering from biological cell. From the Clausius-Clapeyron equation (Yu, No date)

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_2 - V_1)} \tag{3.12}$$

Where ΔH is the molar heat of vaporization, V_1 is the volume of one mole of liquid, and V_2 is the volume of one mole of vapor. If the vapor is considered as an ideal gas, then from ideal gas equation we have

$$PV = MRT/\mu, \tag{3.13}$$

where R is the gas constant, P is the pressure, T is the temperature, M is the mass of gas, and μ is the molar weight. For one mole of vapor, since $V_2 >> V_1$, Equation (3.12) and (3.13) yield

$$\frac{dP}{dT} = \frac{P\Delta H}{RT^2} \tag{3.14}$$

Integration equation 3.14 gives

$$\ln P = \int \frac{\Delta H}{RT^2} dT + C \tag{3.15}$$

For small temperature change, since the heat of vaporization ΔH is a slow-changing function of temperature and ΔH can be taken to be constant, Equation (3.13) can be solved as

$$\ln P = -\frac{\Delta H}{RT} + C \tag{3.16}$$

or

$$\ln P = \mathrm{A} - \mathrm{B}/T \tag{3.17}$$

where A and B are constants (to be determined by experiment), and T is the absolute temperature. This is an approximate expression usually used to relate vapor pressure to temperature. When the vapor pressure is known at several temperatures, the vapor pressures at other temperatures can be determined. Conversely the temperature at the phase equilibrium can be determined from the vapor pressure.

When a cell or callus is suddenly exposed to vacuum, evaporation of water removes considerable heat and hence temperature of the cell or callus rapidly decreases. When phase equilibrium is reached, the temperature at the interface of the two phases is below 0^{o}C. Thus the water at the cell or callus surface will freeze to form an ice shell. For fixed vacuum pressure (i.e. the vapor pressure remains fixed), the temperature of the ice shell surface is constant. This is equivalent to cooling the cell or callus in a constant temperature cooling liquid. The water in the cell as a whole will also freeze after a certain periodical of time that is determined by the thermal conductivity.

For ion implantation experiments in living biological organisms, because the inner water is already frozen during the pumping process prior to the ion implantation, the target can be thought of as a crystal. The crystal is not a perfect crystal; it is divided into many small units. Some units contain more water and thus can be frozen normally; some such as the gas diffusion channels contain less water and so may not be blocked by ice. Water molecules continually evaporate into the vacuum. That mean water is the most of organism that can detect. When incident ions bombard to cell, if the energy from the collision is enough and system is in the proper state , solid organism in biological cell can be changed into the gas phase and thus can detected by quadrupole gas analyzer.