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Wood, Blake P.

Publication Date

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4. Fundamentals of Plasma Immersion Ion Implantation and Deposition

Blake P. Wood, Donald J. Rej, André Anders, Ian G. Brown, Richard Faehl, Shamim M. Malik, and Carter P. Munson*

4.1 Introduction

As discussed in the preceding chapters, conventional ion implantation, chemical vapor deposition (CVD), and physical vapor deposition (PVD) are well-developed technologies used to modify the surface properties of a wide range of materials. A fundamental limitation to more widespread use of ion implantation for large-area, high-dose applications is the time, expense, and complexity associated with conventional line-of-sight, accelerator-based techniques. Plasma immersion ion implantation (PIII) has the potential of overcoming many of the limitations of traditional beamline methods by producing a high dose of ions in a simple, fast, efficient, and cost-effective manner. However, PIII suffers from limitations of its own. The principal advantages and limitations of PIII with respect to conventional beamline implantation are summarized in Table 4.1.

The basic PIII process is illustrated in Figure 4.1. A negative high-voltage pulse, up to 150 kV and over a period between 1 and 150 µs, is applied to an electrically conducting workpiece which is immersed in a plasma. As will be discussed in detail in Chapter 7, a variety of plasmas can be used in PIII&D, including weakly-ionized discharges created from gaseous precursors

* Coordinating Author

admitted into a vacuum chamber, or nearly fully ionized cathodic arc plasmas. Plasma ions are accelerated by the applied electric potential and are implanted into the surface of the workpiece.

In this chapter on PIII&D basics, we will review the time-dependent plasma sheath physics associated with PIII, building on the fundamentals of plasma physics and stationary sheaths developed in Chapter 2. To take full advantage of the non-line-of-sight and conformality properties of PIII, it is important to maintain a sheath thickness which is small compared to the characteristic feature size being implanted. As discussed below, for some situations this cannot be easily accomplished because pulsed power supplies (Chapter 8) are not usually capable of driving the relatively low load impedance that results from small sheaths. Implant uniformity associated with the conformality of the plasma sheaths around complicated geometries will be illustrated in this chapter through a series of supercomputer simulations (§ 4.5).

PIII cannot provide a precise, monoenergetic ion energy spectrum since ion charge and mass separation are not possible, and because the finite pulse rise time and collisional effects smear out the energy spectrum (§ 4.2).

An important feature associated with PIII&D processes is the emission of secondary electrons. The emitted negative electrons are accelerated away from the workpiece in the same electric field that accelerated the positive ions toward the workpiece. Electron emission is a complex function of the bombarding ion energy and species, and the work function and temperature of the workpiece material. We will discuss the role of secondary emission from the surface of the workpiece and its implication for the high-voltage pulser (§ 8) and X-ray production (§ 4.3).

Performing PIII&D inside a bore hole or a cavity is an essential process for many industrial components such as cylinders, dies, and bushings. In the case of bore holes or cavities, the plasma fills the cavity in the workpiece and when the high voltage pulse is applied to it, the ions inside the cavity accelerate to its inner surface. Some of the details of this process are different from "exterior" PIII&D, and therefore a subchapter has been devoted to these issues (§ 4.4).

Although one would assume that PIII&D is limited to conducting substrates and workpieces, ion implantation and deposition can also sometimes be done into and onto non-conducting materials, by biasing the substrate holder or back-electrode. Details are discussed in § 4.6.

As in conventional beamline implantation, the modified surface layer in PIII is relatively shallow, usually less than 100 nm. Deeper layers are achieved by hybrid processes where PIII is combined with other methods such as thermal diffusion (§ 4.7). Depending on plasma processing conditions, one can also deposit plasma ions or neutrals as a thin film before, during, and/or after the PIII pulse using conventional plasma-enhanced CVD or PVD methods, or novel processes such as Metal Plasma Immersion Ion Implantation and Deposition (MePIIID, see § 4.8). For example, PIII has been also used to enhance the films deposited by sputtering of various materials such as titanium, tantalum, and chromium. This process is known as Ion Beam Assisted Deposition (IBAD), Ion Beam Enhanced Deposition (IBED), or Ion Assisted Deposition (IAD).

Throughout this book, PIII refers to plasma immersion processes without film formation while PIIID is used when film deposition is included. The acronym PIII&D is used generically for both processing methods.

4.2 Transient Sheaths

4.2.1 Introduction to Transient Sheaths

The basic physics of plasma sheaths has been reviewed in § 2.2, with emphasis on steady-state conditions. In this section, we consider transient sheaths which are characteristic for PIII&D processes.

When a sudden negative voltage $-V_0$ is applied to the workpiece, electrons near the surface are driven away on a timescale of order the inverse electron plasma frequency ω_{pe}^{-1}, leaving the ions behind to form an ion matrix sheath, i.e., an electron-depleted sheath of not-yet accelerated ions. Subsequently, on a timescale of order the inverse ion plasma frequency ω_{pi}^{-1}, ions within the sheath are accelerated into the workpiece. The consequent drop in ion density in the sheath drives the sheath-plasma edge further away, exposing new ions to the accelerating electric field of the sheath and causing these ions to be implanted. The time evolution of the transient sheath determines the implantation current and the energy distribution of implanted ions. On a longer timescale, the system evolves toward a steady state Child Law sheath (see § 2.2.3.2), with the sheath thickness given by $s = \frac{\sqrt{2}}{3}\,\lambda_{De}\left(\frac{2\,V_o}{T_e}\right)^{3/4}$. This is larger than the matrix sheath by a factor of order $\left(V_0/T_e\right)^{1/4}$, where T_e is the electron temperature given in volts; λ_{De} is the electron Debye

length. This steady state can be of interest in PIII&D for low voltage implantations from high density plasmas.

In the following section, a planar, collisionless transient sheath model will be presented, which allows calculation of sheath thickness, sheath velocity, implant current, and implant dose, under certain simplifying assumptions. After some physical intuition has been developed with a simple model of the transient sheath, we will consider a variety of extensions to the model, which relax some of these assumptions.

1. Cylindrical and spherical sheaths
2. Ions initially present in the ion matrix sheath.
3. Finite rise and fall time of the implant pulse.
4. Ion transit time across the sheath.
5. Collisional effects in the sheath.
6. Multiple ion mass and charge state.
7. Initial standoff of the plasma from the workpiece with pulsed plasma production.
8. Closely spaced sequential implant pulses.

Implantation inside a cylindrical bore is considered in § 4.4.

In general, all of these factors affect sheath propagation, implantation current, and ion energy distribution. Generally, only simple results will be quoted for these extensions. More complicated results and their derivations can be found in the references given.

4.2.2 Collisionless Sheath Model

Figures 4.2(a)-(d) show the time evolution of the sheath in planar PIII geometry. A workpiece is immersed in a uniform plasma of density n_0. At time t=0, a voltage pulse of amplitude $-V_0$ is applied to the workpiece, and the plasma electrons are driven away to form the matrix sheath, with sheath edge at $x=s_0$ (Fig 4.2(b)). As time evolves, Figs. 4.2(c) and (d), ions are implanted, and the sheath edge recedes, leaving a non-uniform, time-varying ion density near the workpiece.

The model assumptions are:

1. The ion flow is collisionless. This is valid for sufficiently low gas pressures.
2. Electrons have zero mass, and thus respond instantaneously to applied potentials. This follows because the characteristic implantation timescale much exceeds ω_{pe}^{-1}.
3. The full voltage $-V_0$ is applied at $t=0$, and is much greater than the electron temperature T_e; hence $\lambda_{De} << s_0$, and the sheath edge at s is abrupt.
4. A quasistatic Child Law sheath forms instantaneously. The current demanded by this sheath is supplied by the uncovering of ions at the moving sheath edge.
5. The ion transit time across the sheath is zero, that is, the implant current equals the charge uncovered by the expanding sheath.
6. Ions are singly charged.

The Child Law current density j_c for a voltage V_0 across a sheath of thickness s is given by

$$j_c = \frac{4}{9}\varepsilon_0\left(\frac{2e}{M}\right)^{1/2}\frac{V_0^{3/2}}{s^2} \tag{4.2.1}$$

where ε_0 is the free space permittivity and e and M are the ion charge and mass. Equating j_c to the charge per unit time crossing the sheath boundary, $en_0\, ds/dt$, we find the velocity of the sheath edge ("sheath velocity")

$$\frac{ds}{dt} = \frac{2}{9}\frac{s_0^2\, u_0}{s^2} \qquad (4.2.2)$$

where

$$s_0 = \left(\frac{2\,\varepsilon_0\, V_0}{e\, n_0}\right)^{1/2} \qquad (4.2.3)$$

is the ion matrix sheath thickness and $u_0 = (2eV_0/M)^{1/2}$ is the characteristic ion velocity. It is worth noting that the sheath velocity can be highly supersonic for high applied voltages and low density plasmas. Integrating (4.2.2), we obtain the sheath position

$$s = s_0\left(1 + \frac{2}{3}\omega_{pi}\, t\right)^{1/3} \qquad (4.2.4)$$

where $\omega_{pi} = (e^2 n_0/\varepsilon_0 M)^{1/2} = u_0/s_0$ is the ion plasma frequency. Plugging (4.2.4) back into the Child Law current density yields the implant current density

$$j = \frac{2}{9}\frac{e\, u_0\, n_0}{\left(1+\frac{2}{3}\omega_{pi} t\right)^{2/3}} = \frac{4}{9}\frac{\varepsilon_0\, u_0\, V_0}{s_0^2\left(1+\frac{2}{3}\frac{u_0}{s_0}t\right)^{2/3}}. \qquad (4.2.5)$$

The charge per unit area σ_p implanted in a single pulse can be found by integrating (4.2.5) over the pulse duration t_p

$$\sigma_p = \frac{2\,\varepsilon_0\, V_0}{s_0}\left[\left(1+\frac{2}{3}\omega_{pi} t_p\right)^{1/3} - 1\right] \qquad (4.2.6)$$

Utilizing normalized units for the current density, sheath width, and time, $J = j/(en_0 u_0)$, $S = s/s_0$, and $T = \omega_{pi}\, t$, respectively, equations (4.2.4) and (4.2.5) can be expressed [1]

$$S(T) = \left(1 + \frac{2}{3}T\right)^{1/3} \tag{4.2.7}$$

$$J(T) = \frac{2}{9}\frac{1}{S^2} = \frac{2}{9}\left(1 + \frac{2}{3}T\right)^{-2/3}. \tag{4.2.8}$$

4.2.3 Extensions to the Collisionless Sheath Model

4.2.3.1 Cylindrical and Spherical Sheaths

Scheuer *et al.* [2] derived expressions for the propagation of the sheath edge (i.e. sheath thickness) and ion current in cylindrical and spherical geometries. These expressions depend on the ratio of sheath radius to object radius, and must be solved numerically.

In the cylindrical case, the Child Law current density (in this case, the current per unit area of expanding sheath) is [3]

$$j_c = \frac{4}{9}\,\varepsilon_0 \left(\frac{2e}{M}\right)^{1/2} \frac{V_0^{3/2}}{r\, r_w\, \beta^2}, \tag{4.2.9}$$

where r is the radius of the sheath edge, r_w is the workpiece radius, and β is a dimensionless function of (r/r_w) which can be expanded as [4]

$$\beta = \gamma - \frac{2}{5}\gamma^2 + \frac{11}{120}\gamma^3 - \frac{47}{3300}\gamma^4 + \ldots, \tag{4.2.10}$$

where $\gamma = \ln(r/r_w)$. The first four terms of this series are sufficient to give β to an accuracy of 1.1% for $(r/r_w) = 5$, but this approximation rapidly diverges from the exact result for $(r/r_w) > 5$. The first 10 coefficients of this series are given in Table 4.2.

Assuming (as we did in the planar case) that ions are supplied by the expanding sheath, and switching to normalized coordinates, the equation for the sheath expansion becomes

$$\frac{dR}{d\theta} = \frac{1}{R\,\beta^2}, \qquad (4.2.11)$$

where $\theta = \frac{4\sqrt{2}}{9} A^{3/2} \omega_{pi} t$, $R = r/r_w$, and $A = \left(eV\,\lambda_{De}^2\right) / \left(kT_e\, r_w^2\right)$; the quantities eV and kT_e must obviously be given using the same units, usually in electron volts (eV). Conrad [5] derived an approximate ion matrix sheath width, which in these units becomes

$$R_0^2 \cong \left[(2A)^{1/2} + 1\right]\left[(3A)^{1/3} + 1/2\right] \qquad (4.2.12)$$

The position of the sheath edge can then be determined by integrating the equation

$$\int_{R_0}^{R_f} R\beta^2(R)\, dR = \theta_f - \theta_0 \qquad (4.2.13)$$

where θ_f is calculated at the desired time, and θ_0 is taken to be zero at the initial time t=0.

The spherical case is similar, with (4.2.9) – (4.2.13) replaced respectively by

$$j_c = \frac{4}{9}\varepsilon_0 \left(\frac{2e}{M}\right)^{1/2} \frac{V_0^{3/2}}{r^2 \alpha^2}, \qquad (4.2.14)$$

$$\alpha = \gamma - \frac{3}{10}\gamma^2 + \frac{3}{40}\gamma^3 - \frac{63}{4400}\gamma^4 + \ldots, \qquad (4.2.15)$$

$$\frac{dR}{d\theta} = \frac{1}{R^2 \alpha^2}, \qquad (4.2.16)$$

$$R_0 \cong (3A)^{1/3} + 1/2, \qquad (4.2.17)$$

$$\int_{R_0}^{R_f} R^2 \alpha^2(R) dR = \theta_f - \theta_0, \qquad (4.2.18)$$

where the expansion for α is given in [3], with the first 10 coefficients of the series given in Table 4.2, and the current density j_c is current per unit area of expanding sheath.

For objects of similar radius of curvature and similar total areas, and for equivalent plasma and pulse parameters, the sheath is thinner and the current density higher in cylindrical geometry than in planar geometry; more so in spherical geometry. This is shown in Figure 4.3, which presents a dimensional plot of sheath width calculated from Eqs. (4.2.4), (4.2.9) – (4.2.13), and (4.2.14) – (4.2.18), compared with results from particle-in-cell (PIC) simulations performed with the codes PDP1, PDC1, and PDS1 [6].

4.2.3.2 Depletion of the Ion Matrix Sheath

The collisionless sheath model assumes that the quasistatic Child Law sheath is instantaneously produced. It neglects implantation of the ions initially present in the ion matrix sheath. Lieberman [7] has analyzed the effect of these ions upon the transient sheath, also including the effect of ions approaching the expanding transient sheath at the Bohm velocity $u_B = (kT_e/M)^{1/2}$, as produced by a plasma presheath. He derives two solutions in planar geometry, one valid during the depletion of the ion matrix sheath, and the other valid at later times when a quasistatic Child Law sheath is present. The transition between these two solutions occurs approximately at $\omega_{pi}t = 2.7$. During the depletion of the ion matrix sheath, the normalized current density is

$$J(T) = \frac{\sinh T}{\cosh^2 T} + \frac{2}{9}\frac{1 + T\sinh T - \cosh T}{\cosh^2 T}, \tag{4.2.19}$$

where $J = j/(en_0u_0)$, and $T = \omega_{\text{pi}}t$. The solution for later times requires numerically solving the pair of equations

$$T = \frac{3}{2}\left(\frac{x_0}{s_0}\right)^3 + 3\left(\frac{x_0}{s_0}\right) - \frac{3}{2} \tag{4.2.20}$$

$$J = \left[\frac{9}{2} \left(\frac{x_0}{s_0} \right)^2 + 3 \right]^{-1} \qquad (4.2.21)$$

which give *J(T)* as a parametric function of x_0/s_0, where s_0 is the matrix sheath width, and x_0 is the initial position of an ion which is implanted at a time *t*. Lieberman also derives parametric equations for the energy distribution of implanted ions during the depletion of the ion matrix sheath, the expansion of the quasistatic Child Law sheath, and the stragglers which are implanted after the implantation pulse is turned off. The ions in the ion matrix sheath ($x_0 \leq s_0$) are implanted with energy

$$W = V_0 \left\{ 1 - \left[(s_0 - x_0)^2 / s_0^2 \right] \right\} \qquad (4.2.22)$$

yielding an energy distribution of

$$\frac{dN}{dW} = \frac{n_0 \, s_0}{2 \, V_0^{1/2}} (V_0 - W)^{-1/2}. \qquad (4.2.23)$$

Ions in the interval $s_0 \leq x_0 \leq x_T$ are implanted at full energy, where x_T is the initial position of an ion which reaches the workpiece at the time the pulse is shut off, as calculated from (4.2.20).

Ions in the interval $x_T \leq x_0 \leq s_T$, where s_T is the position of the sheath when the pulse is shut off, are in flight when the accelerating potential disappears, and so are implanted at a lower energy given by

$$W(x_0) = V_0 \left\{ 1 - \left[(s_T - x_0) / s_T \right]^{5/3} \right\} \qquad (4.2.24)$$

where s_T is given by

$$\frac{3}{2} \left[\left(\frac{s_T}{s_0} \right)^3 - 1 \right] = T, \qquad (4.2.25)$$

yielding an energy distribution

$$\frac{dN}{dW}=\frac{2}{5}\frac{(s_T-x_T)n_0}{V_0^{2/5}}(V_0-W)^{-3/5}. \qquad (4.2.26)$$

4.2.3.3 Finite Rise and Fall Times

The collisionless sheath model assumes zero rise and fall times for the implantation pulse. Stewart and Lieberman [8] have derived a model for finite rise and fall times in planar geometry, under the assumptions that the quasistatic Child Law sheath forms instantaneously, the voltage rises and falls linearly, and ions have no directed velocity toward the expanding sheath. In the normalized units described above, with the normalized sheath width $S=s/s_0$, and T_r, T_p, T_f, and T_t representing the normalized rise, flat-top, fall, and total times, respectively, they derive the following three equations for sheath width:

$$S(T)=\left(\frac{4}{15}\right)^{1/3}\frac{T^{5/6}}{T_r^{1/2}}, \quad 0<T<T_r, \qquad (4.2.27)$$

$$S(T)=\left[\frac{2}{3}\left(T-\frac{3}{5}T_r\right)\right]^{1/3}, \quad T_r<T<T_r+T_p, \qquad (4.2.28)$$

$$S(T)=\left[\frac{2}{3}T_p+\frac{4}{15}(T_r+T_f)-\frac{4}{15}(T_t+T)^{5/2}\Big/T_f^{3/2}\right]^{1/3}, \quad T_r+T_p<T<T_t. \qquad (4.2.29)$$

Stewart and Lieberman (1991) also derive parametric equations for the normalized implant current density *J(T)*, and the implanted ion energy distribution. Figure 4.4 contrasts the normalized planar implant current density from the models of Scheuer and co-workers [2], Eq. (4.2.8); Lieberman [7], equations (4.2.19)-(4.2.21); and Stewart and Lieberman [8] with results obtained from a particle-in-cell (PIC) simulation using the code PDP1 [6]. The Stewart and Lieberman equations require a normalized rise time T_r to be specified. In Figure 4.4, a value of T_r = 2 is used, which corresponds to a 0.25 μs rise time in a 10^{15} m^{-3} N_2^+ plasma. Similar

parameters have been used in the PIC simulation. The initial current peak for the Lieberman model is greater than given by the simulation, because it assumes an instantaneous voltage rise time. That of the Stewart and Lieberman model is below the simulation result because it assumes instantaneous establishment of a space charge limited ion flow, in other words, zero ion transit time across the sheath and zero displacement current. This assumption will be examined more closely in the next section.

4.2.3.4 Ion Transit Time Across the Sheath

Wood [1] examines the situation where ion transit time across the sheath is significant with respect to the sheath expansion. The accelerating potential is dropped almost linearly across the sheath in the limit of very low ion density, as exists in high potential Child Law ion flow. If the sheath expands significantly during an ion transit time, the ion will not experience the full accelerating potential. Wood also points out that, particularly early in time when the ion matrix sheath is being depleted, the implant current does not equal the rate of ions uncovered by the expanding sheath, as assumed in the collisionless transient sheath model. This discrepancy is accounted for by the displacement current produced by the changing electric field in the sheath, as represented in the complete current continuity equation

$$\nabla \cdot \left(J + \varepsilon_0 \frac{\partial E}{\partial t} \right) = 0 . \qquad (4.2.30)$$

Asserting that conduction current is conserved across the sheath is equivalent to ignoring the $\partial E / \partial t$ term in (4.2.30). As long as the sheath is expanding, this term will be non-zero. Since the sign of the displacement current term is opposite that of the conduction current term, the conduction current (equivalently, the implant current in the absence of secondary electrons) is

higher than calculated from the uncovering of ions by the expanding sheath. Wood presents a parametric equation for the energy of implanted ions in the quasistatic Child Law sheath. Numerical simulations are presented that suggest that this effect is only important for high-voltage PIII from plasmas of low density, in the 10^{14}–10^{15} m^{-3} range.

4.2.3.5 Collisional Effects

Vahedi *et al.* [9] has modeled the planar transient sheath in the highly collisional limit, with ion-neutral charge exchange being the dominant collision. Under this assumption, the ion density in the sheath is constant spatially, somewhat lower than that in the bulk plasma, and slowly decreasing with time as the sheath expands. By examining the probability that an ion created at rest some distance from the workpiece will be implanted before suffering another charge exchange collision, the mean ion velocity and implant current density are derived to be

$$\langle u \rangle = \left(\frac{eV_0\, \pi\, \lambda_i}{M\, s} \right)^{1/2}, \qquad (4.2.31)$$

$$j = \varepsilon_0 \left(\frac{4\pi\, e\, \lambda_i}{M} \right)^{1/2} \frac{V_0^{3/2}}{s^{5/2}}, \qquad (4.2.32)$$

where the sheath width s is

$$s(t) = s_0 \left(1 + \frac{7u_0}{2s_0} t \right)^{2/7}, \qquad (4.2.33)$$

with the initial sheath thickness s_0 given by (4.2.3), characteristic ion velocity in the sheath $u_0 = \left(eV_0 \pi \lambda_i / M s_0 \right)^{1/2}$, and charge-exchange mean-free-path λ_i. Wang [10] has used this model to derive a velocity distribution for the fast neutrals created in ion-neutral charge-exchange collisions, under the assumption that fast neutrals suffer no further collisions after their creation.

Vahedi *et al.* [11] also developed an analytic model for the angular distribution of ions hitting the workpiece after transiting a collisional sheath, under the assumptions that ions suffer exactly one scattering collision after their final charge exchange collision, and that the scattering and charge exchange cross sections are independent of ion energy. It is found that the total scattered flux of ions at the workpiece ($z = 0$) is

$$\Gamma_{0,z=0} = \int_0^{\pi/2} d\theta' \Gamma'(\theta'), \tag{4.2.34}$$

where

$$\Gamma'(\theta') = \int_0^{u_{m0}\cos\theta'} v' dv' \times \int_0^{z_{\max}(v',\theta')} dz\, e^{-zn_0\sigma_T} \Gamma_1(v',\theta'), \tag{4.2.35}$$

and

$$\Gamma_1(v',\theta') = \frac{2s\Gamma_0\sigma_{scat}}{\lambda_T u_{m0}^2} \frac{v'^2 \sin\theta' \cos\theta'}{v'^2\cos^2\theta' - 2V(z)/M} \times \exp\left(-\frac{s}{2\lambda_T u_{m0}^2} \frac{\left[v'^2 - 2V(z)/M\right]^2}{v'^2\cos^2\theta' - 2V(z)/M} \right). \tag{4.2.36}$$

In equations (4.2.34) – (4.2.36), λ_T is the total ion-neutral mean free path, including both scattering and charge exchange collisions, σ_{scat} and σ_T are the scattering and total (scattering plus charge exchange) ion-neutral cross sections, respectively, V_0 is the applied potential on the workpiece, $V(z)$ is the local potential with respect to the workpiece potential, $u_{m0}^2 = 2eV_0/M$ is the square of the velocity the ion would have at the workpiece if it had suffered no collisions , s is the sheath width, Γ_0 is the total incident ion flux, n_0 is the neutral density, θ' is the angle from normal of the ion, and v' is the ion velocity, where the prime denotes values at the workpiece. The upper limit of the z-integration in (4.2.35), $z_{\max}(v',\theta')$, is the farthest distance from the workpiece of the last charge exchange collision, and is derived to be

$$z_{\max}(v',\theta') = s\left(1 - \frac{1-(v'/u_{m0})^2}{\left[1-(v'/u_{m0})^2(2-\cos^2\theta')\right]^{1/2}}\right). \quad (4.2.37)$$

Since there is an assumption that $\lambda_{scat} > \lambda_{cx}$, there will be a delta function in the flux at $\theta' = 0$. It is found that in the case of $\lambda_T << s$ and $\lambda_{scat} >> \lambda_{cx}$, the average angle of the scattered ions is constant and ≈ 20°, while the average angle for all ions is typically < 1°. These equations are found to be in good agreement with particle-in-cell simulations over a wide range of pressures (0.1-10 Pa, or 1-100 mTorr) at a moderate voltage (500 V) for an atomic hydrogen plasma.

4.2.3.6 Multiple Ion Mass and Charge State

Qin and co-workers [12] have extended the planar collisionless transient sheath model to take into account the effect of a plasma containing several ion species of varying masses and charge state. It is shown that equation (4.2.4) for sheath propagation can be used, with the ion mass M in the ion plasma frequency ω_{pi} replaced by an equivalent mass is given by

$$\sqrt{M} = \sum_j k_j \sqrt{Z_j M_j}\ , \quad (4.2.38)$$

where j is the ion index, Z_j and M_j are the charge state number and mass, respectively, of the jth ion, and k_j is the fraction of the total ion density for the jth ion defined as

$$k_j = \frac{n_j}{\sum_Z Z\, n_Z}, \quad (4.2.39)$$

where n_Z is the ion density of ions with charge state Z.

Multiple ion masses frequently occur with molecular gas plasmas while multiple charge states are characteristic for cathodic arc and laser ablation plasmas. If multiply charged ions are

present, the electric current associated with a particle current is $j_{elec} = \bar{Z}\, j_{part}$ where $\bar{Z}$ is the mean ion charge[†] (§ 4.8.2.4).

4.2.3.7 Initial Standoff of the Plasma from the Workpiece with Pulsed Plasma Production

When the plasma production is pulsed and synchronized with the implant pulses applied to the workpiece, as is sometimes done with vacuum arc plasmas [16] and inductively coupled plasmas [17], the time delay between plasma production and implantation can be adjusted to affect the implant current and implanted ion energy distribution. This effect has been examined with particle-in-cell simulation and laboratory experiment [18]. It is found that if the implant pulse is applied to the workpiece when there is still some standoff between the workpiece and plasma, a higher proportion of ions are implanted at the full energy, because most of the applied potential is dropped across the region between the workpiece and plasma. In addition, the very high implant current typically seen early in the implant pulse (see Figure 4.4), resulting from depletion of the ion matrix sheath, is reduced, thereby lessening the load on the modulator and potentially shortening the rise time of the implant pulse. Experimental evidence of the reduction in peak implant current is presented in Figure 4.5.

4.2.3.8 Sheath Evacuation and Replenishment

[†] Sometimes in the literature, e.g. in [13-15], not Z but the symbol Q is used for the ion charge state in order to clearly distinguish this quantity from the element's atomic number. The reader should not confuse these quantities.

Plasma Immersion Ion Implantation (PIII) is effectively an ion pump, implanting ions from an expanding sheath region during a high voltage workpiece pulse, and allowing the plasma to replenish this region between pulses. Most models of the sheath physics in PIII consider the effect of a single voltage pulse, under the assumption that the ions have time between pulses to flow back into the depleted region near the workpiece. We will now examine the effect of multiple pulses when the pulse frequency is sufficiently high and the sheath width sufficiently wide that ion diffusion cannot replenish the depleted region between pulses. This situation can exist in the low density (10^{14}-10^{16} m^{-3}) gaseous plasmas commonly used when implanting large areas (> 1 m^2). In this case, the sheath widths and implant currents established after many pulses are very different than those after a single pulse. This effect has been examined by Wood [1].

At the end of a PIII pulse, the sheath collapses as the workpiece voltage falls. The fall time is determined by the rate at which the induced workpiece surface charge and any charge stored in external circuit capacitance can be discharged through the external circuit. As the sheath collapses, the electron density only “fills up” to the local ion density, which has been depleted near the workpiece during the pulse. This leaves a steep gradient in quasi-neutral plasma density. If the repetition rate is sufficiently high and the sheath sufficiently wide, there is not time between pulses for the plasma to diffuse back into the depleted region. This is illustrated in Figures 4.6(a)-(c), which show a particle-in-cell simulation [6] of the ion density profiles at 1 μs intervals resulting from two 10 μs pulses (with 1 μs rise and fall times) separated by a 20 μs off period (this pulse frequency is much higher than that used in most PIII facilities, to show the effect clearly). In Figure 4.6(a), a space-charge limited flow is established and the sheath expands to 0.37 m during the first pulse. During the off period, shown in Figure 4.6(b), the

plasma flows into the region depleted by the first pulse (only the ions are shown). The sheath formed by the second pulse, shown in Figure 4.6(c), expands into a very different plasma than did the first pulse. The lower plasma density in the depleted region allows the sheath to expand more quickly and to a greater width than during the first pulse. The sheath reaches 0.48 m by the end of the second pulse. The sheath widths during the first three pulses, shown in Figure 4.7, increase with each pulse. Figure 4.8 shows the ion implant current at the workpiece for the same three pulses. The initial high current of the first pulse is unique, corresponding to the evacuation of the ion matrix sheath. Later pulses start with an ion density profile which is similar to that produced by a space-charge limited flow.

How important is this effect? In the case of a collisionless sheath, the flow of non-drifting ions into the depleted region will be at the ion thermal velocity with an ambipolar enhancement due to the presence of electrons at a temperature much higher than the ions.

Modeling the plasma density as a step function at s, the location of the maximum sheath width from the previous pulse, with a spatially constant density n_s in the depleted region and a density of n in the plasma, Wood [1] has calculated that the depleted region fills in according to the equation

$$\frac{n_s(t)}{n} = 1 - \left(1 - \frac{n_{s0}}{n}\right) e^{-\vartheta t}, \qquad (4.2.40)$$

where the fill-in rate (per second) is $\vartheta = (T_e / T_i) \frac{1}{s} (kT_i / 2\pi M)^{1/2}$ and n_{s0} is the initial density in the depleted region. Assuming $n_{s0}=0$, the depleted region will fill in to 95% of the plasma density in a time $t_{95\%} = 3/\vartheta$. A plot of $t_{95\%}$ versus s is shown in Figure 4.9, for ion temperatures of 0.026,

0.1, and 0.26 eV. The time to fill in the depleted region increases with higher T_i because the ambipolar enhancement decreases faster than the increase in unenhanced u_i. In cylindrical or spherical geometries the depleted region will fill in more quickly than shown in Figure 4.9, because the sheath will be thinner for an equivalent workpiece pulse and the sheath area over which ions flow will be relatively larger per volume of depleted region.

The pulse-to-pulse increase in the sheath width shown in Figure 4.7 cannot go on indefinitely. A multiple-pulse steady-state will be established in which the charge flowing continuously into the depleted region is completely swept out during the pulse. In a planar geometry, this current will be independent of sheath width, to the extent that $n_s/n \ll 1$ at all times, i.e., that the depleted region does not fill in significantly between pulses. In cylindrical or spherical geometries this will not be the case, since the sheath area depends on the sheath width.

When the workpiece voltage pulse turns off in PIII, a disturbance caused by the sharp density gradient will propagate into the plasma. This is seen in Figure 4.6(b) as an additional depletion of neutral plasma beyond the maximum sheath width. If the depleted region does not fill in completely during the off-time, the depletion beyond the maximum sheath width in the multiple-pulse steady-state will form a presheath. We will assume that this presheath gives ions at the maximum sheath width a directed velocity of $u_B = (kT_e/M)^{1/2}$, although the actual velocity will likely depend on the specific pulse duty cycle used. This directed velocity produces an ion flux into the depleted region of $\Gamma = 0.6 n u_B$, yielding an estimate for the time-average implant current of

$$i_B = 0.6\, A\, e\, n \left(\frac{kT_e}{M} \right)^{1/2} . \qquad (4.2.41)$$

Note that this is equal to the space-charge limited current that would exist across the very large sheath produced by applying the workpiece voltage as a DC signal. PIII can be considered an ion pump that removes in a short time the ions that accumulate in the depleted region over a longer time.

To summarize, if the pulses are repeated at a high enough frequency that the depleted region around the workpiece is not repopulated with ions between pulses, a steady-state will be established in which the expanding sheath during each pulse will just sweep out the ions which continuously flow into the sheath region. The resulting maximum sheath width will be larger and the peak implant current smaller than for initial pulses. This effect will be most pronounced for low density plasmas due to the large resulting sheaths and small particle fluxes.

This work suggests that in an experimental system with a given maximum current, the plasma density should be made higher than analysis of a single pulse would indicate. Most high-power pulse modulators behave more like constant-current sources than the constant-voltage sources commonly used in models. Consequently, choosing the plasma parameters to provide a good match to the power source in the multiple-pulse steady-state will slow the voltage rise time in the initial pulses, resulting in ion energies below the design goal. However, the multiple-pulse steady-state will be reached in a very small fraction of the time required for the total implant, so this will not affect the finished product.

4.3 Secondary Electron Emission

An important feature associated with PIII is the emission of secondary electrons produced during ion implantation. The high-energy ions which strike the workpiece surface deposit a large amount of energy in the near surface layer. Some of this energy causes the emission of electrons from the workpiece surface. Since the ions and electrons have opposite charge, the emitted negative electrons are accelerated away from the workpiece in the same electric field that accelerated the positive ions toward the workpiece. The electron emission coefficient γ_{SE} (number of electrons emitted per incident ion) can be quite large. For example, for a 20 keV N^+ ion incident on stainless steel, γ_{SE} = 4.8, with much higher values reported for aluminum. The emission coefficient varies roughly linearly with the square root of ion energy [19]. Measured secondary electron coefficients for argon and nitrogen ions on a variety of materials in a PIII experiment are shown in Tables 4.3 and 4.4 [20]. These coefficients are generally much greater than published data for low-current experiments with atomically clean surfaces (see, e.g., [21]). In most PIII situations, surfaces are not atomically clean, and the momentary current density can be much higher than what has been used for measurements published in the literature. More research is needed to elucidate the influence of these conditions.

This current of high energy electrons causes several problems. First, the flow of ions and electrons both represent current that must be provided by the high-voltage power supply:

$$I_{total} = I_i + I_{SE} = (1 + \gamma_{SE}) I_i \qquad (4.3.1)$$

If γ_{SE} = 10, then 91% of the current is carried by the electrons while only 9% of the current is ion flow to the workpiece. This requires a much larger power supply than would be needed to supply the ion current alone. Furthermore, these emitted electrons are accelerated and strike the vacuum chamber wall where they deposit heat, which must be removed by active cooling in high

power systems, and create X-rays, which require additional lead shielding in high-voltage systems [22], see also §§ 6.7.4 and 9.3.3. Modeling and experimentation has shown that the X-ray flux, and hence the requirements for shielding, increases as a very steep function (a power of 4-5) of the implant energy [22, 23].

A technique used to suppress secondary electron X-ray generation is illustrated in Fig. 4.10 [24]. Secondary electrons are trapped within a metal enclosure supported from the vacuum chamber walls, which is biased to the same electrical potential as the workpiece. A remote plasma source produces a plasma near ground potential. When voltage is applied to the workpiece, it also is applied to the entire enclosure. The applied voltage develops across a sheath between the plasma and the workpiece, and also between the plasma and the enclosure. Therefore, ions are implanted into both the workpiece and the enclosure. Secondary electrons emitted from the workpiece and the enclosure are repeatedly reflected within the interior of the enclosure, and they are prevented from impacting the grounded vacuum chamber walls. The only grounded surface available for X-ray production is the plasma source, whose area can be minimized. Recent experiments using this technique at the Hughes Research Laboratory at 50 kV voltage levels (see Table 4.5), have reduced the X-ray level from 20 mrad/hour to a level below the minimum detection limit (<0.2 mrad/hour). At 75 kV operation, the X-ray level has been reduced by a factor of four. The remaining X-rays are dealt with shields (§ 9).

A limitation of this suppression method is sputtering of enclosure material. As plasma ions are implanted into the enclosure surface, they sputter enclosure material which, in turn, inevitably gets redeposited onto the workpiece surface. This contamination can be minimized by selecting

enclosure materials that are compatible with or similar to the workpiece, or materials with a low sputter yield. Alternatively, one could envision a PIII-assisted deposition process where enclosure material is intentionally sputtered onto a workpiece during PIII.

There exist other proposed (but unproven) techniques for suppressing secondary electrons. One method involves using negative ions and positive accelerating voltages. Negative ion sources have been developed for high-energy particle accelerators. The extrapolation of these sources to supply the large average currents demanded by PIII remains a challenge; furthermore, maintaining a high negative ion to electron density ratio will be essential to minimize unwanted primary electron currents and X-ray emission. A second method uses multiply-charged ions which will reduce the required acceleration voltage, thereby reducing the power losses, bremsstrahlung X-ray generation, and shielding requirements. Multiply charged ions may be produced by a variety of plasma sources including cathodic arc sources and pulsed RF sources (§ 4.8). A third method, shown in Fig. 4.11, uses an externally applied magnetic field [25]. Secondary electrons are trapped in the field to form a virtual cathode layer near the workpiece surface where the local electric field is substantially reduced. Subsequent electrons that are emitted can then be reabsorbed by the workpiece. The magnitude of the magnetic field is chosen so that secondary electron trajectories are greatly altered, while ion motion is only slightly perturbed.

While the suppression of secondary electrons remains an ongoing part of present-day research, virtually all PIII devices are operated without any secondary electron control. Consequently, an

adequate X-ray shield is an important part of a PIII facility, and will be covered in detail in Chapter 9.

It is possible to use secondary electrons to one's advantage, to enhance plasma density around the workpiece. In low voltage (< 1 kV) PIII situations, it is possible for secondary electrons to directly ionize neutral gas molecules in the chamber. At higher voltages, the electron-neutral ionization mean free path is too long to produce significant additional plasma in reasonable sized chambers ($\lambda_{iz} \approx 30\ \mathrm{m}$ for 10 kV electrons in 0.1 Pa argon) [26], although it is possible, by careful arrangement of the geometry, to extend the electron path sufficiently by multiple reflection from workpiece surfaces so that plasma density can be significantly increased by electron reflexing (hollow cathode effect) [27]. This is not necessarily a desirable operating condition, however, as plasma can be produced in the sheath region, from which ions are implanted at less than the applied workpiece potential.

It is also possible to excite a beam-plasma instability in which secondary electrons resonantly excite plasma waves, which transfer their energy to the bulk plasma through Landau damping. This increases the bulk electron temperature, and leads to an increase in the ionization rate [28, 29]). This effect has been observed in PIII simulations [25] and experiments [27]. This is an advantageous operating condition, since increased plasma density in the bulk plasma will reduce the sheath widths, allowing higher packing densities of workpieces. The fraction of secondary electron energy which can be coupled into the plasma can be estimated as follows [27]. The secondary electron flux in the system is

$$n_s v_s = N_p \gamma_{SE} \Gamma_i, \qquad (4.3.2)$$

where N_p is the number of reflex passes a secondary makes in the system, γ_{SE} is the secondary electron emission coefficient, Γ_i is the ion flux to the workpiece, and n_s and $v_s = (2eV/m_e)^{1/2}$ are the secondary electron density and speed, respectively, with V the applied PIII voltage. The ratio of secondary electron to thermal electron density is

$$\varepsilon = \frac{n_s}{n} = \frac{N_p \, \gamma_{SE} \, \Gamma_i}{n \, v_s}, \tag{4.3.3}$$

which stimulates growth of the plasma waves at a rate [30]

$$\beta = \frac{\sqrt{3}}{2}\left(\frac{\varepsilon}{2}\right)^{1/3} \omega_{pe} , \tag{4.3.4}$$

where ω_{pe} is the plasma frequency of thermal electrons. The fraction, F, of secondary electron energy which can be transferred to the plasma can be approximated by

$$F = \left(\frac{\varepsilon}{2}\right)^{1/3} \left[1 - e^{-\beta\tau}\right], \tag{4.3.5}$$

where τ is the interaction time of secondary electrons with the plasma. This interaction time is typically short in most laboratory experiments, so that $\beta\tau << 1$. In this case, $F \approx (\varepsilon/2)^{1/3} \beta\tau$.

4.4 Implantation in Pipes and Holes

Most PIII work to date has been on the outside surfaces of workpieces. Nevertheless, there is great commercial interest in implanting and depositing coatings on the inside surfaces of pipes and holes. When considering PIII into the inner surfaces of objects, three problems deserve special attention:

1. How is the plasma supplied? If the characteristic dimension of the interior is smaller than several Debye lengths, the plasma will not be uniform, and calculations of characteristic sheath lengths will be difficult. Replenishment of the plasma between PIII pulses (§ 4.2.2.8) will take much longer than in the exterior case, due to the restricted geometry.

2. What happens to the electrons? The ion matrix sheath is established by moving electrons away from the biased electrode. In exterior geometries, this is assumed to be accomplished without increasing the electron density outside the sheath. In a confined, interior geometry, these electrons have to go somewhere, either exiting the volume longitudinally, or locally increasing the electron density, with consequent effects on the plasma. If secondary electrons are produced by the implantation of ions into the interior wall, they too must go somewhere. However they are produced, electrons may reflex between the expanding sheaths, gaining energy and contributing to a hollow cathode effect.

3. Is there enough room for the sheaths? In an exterior geometry, sheaths can expand indefinitely (subject to the dimensions of the vacuum chamber, of course). In an interior geometry, sheaths are expanding toward each other, and may overlap, with consequent effects on the plasma and potentials experienced by particles.

These effects suggest that, unlike exterior geometries where simple PIII sheath models agree well with experimental results, the simple models described in this section should be taken with a grain of salt in the interior case. Nevertheless, it is instructive to examine these models, particularly to understand when the problems described above deserve closer examination.

The ion matrix sheath in a cylindrical bore was examined by Sheridan [31], who characterized two solutions, depending on whether or not the sheaths overlapped at the center of the cylinder. The smallest cylinder for which the sheaths do not overlap has radius

$$d = \sqrt{\frac{4\varepsilon_0 V}{e n_0}}, \tag{4.4.1}$$

where V is the magnitude of the applied PIII voltage, and n_0 is the plasma density. This distance is $\sqrt{2}$ times the ion matrix sheath width in the planar case, given by Eq. (4.2.3). Note, however that Eq. (4.4.1) is **not** the ion matrix sheath width in the interior case, it is only the maximum possible ion matrix sheath width. When the cylinder radius $R > d$, the actual value of the ion matrix sheath width will decrease with increasing cylinder radius, asymptotically approaching the value for the planar case. This decrease occurs rapidly as the radius increases: when $R/d = 1.2$, the sheath width has decreased 50% of the way to the asymptotic planar value, and when $R/d = 6.3$, it has decreased 95% of the way.

When the cylinder radius $R < d$, the sheaths overlap and the potential drop between the cylinder wall and cylinder axis goes as the square of the cylinder radius, that is, if the cylinder radius $R = d/2$, then the potential drop is $V/4$, limiting the maximum implant energy.

Even in the $R > d$ case, the maximum implant energy may be less than the applied potential due to motion of the sheath during an ion transit time, as was discussed for the planar case in § 4.2.2.4. This effect is exaggerated in the interior case, because the sheath velocity is higher than the planar case due to the convergent geometry. Furthermore, unlike the exterior case where the sheath velocity decreases monotonically with time, Sheridan shows that, given a long enough

PIII pulse, an expanding interior sheath reaches a minimum velocity, and then accelerates due to convergent effects near the axis [32], assuming that the equilibrium Child-Langmuir sheath width is larger than the cylinder radius (as will be the case for nearly all high voltage PIII situations). Sheridan derives the maximum normalized ion impact energy to be [33]

$$u_{P,\max}^2 \equiv \frac{1}{2}\frac{Mv_{iR}^2}{eV} \approx \begin{cases} 0.3678P^2, & \text{for } P \le 1, \\ 1 - \dfrac{0.8790}{P^2} + \dfrac{0.2468}{P^4}, & \text{for } P > 1, \end{cases} \tag{4.4.2}$$

where M is the ion mass, v_{iR} is the ion velocity at the sidewall, V is the applied potential, and $P = R/d$ is the dimensionless cylinder radius. The function defined in (4.4.2) is plotted in Figure 4.12. Note that as the cylinder radius increases the result approaches the exterior result of maximum ion impact energy equaling the applied potential.

Sheridan [33] also develops a relationship between the normalized sheath width $W = (P-\sigma)/P$ and normalized time $\Theta = T/\left(9\sqrt{2}\,P^3\right)$ where $\sigma = (R-s)/d$ is the normalized plasma width with s being the sheath width, and $T = \omega_{pi}t$ is the normalized time. For a zero-rise time pulse, this relationship is

$$\theta = \frac{5}{33}\left(1 + \frac{2}{15}W\right)^{5/2}\left(720 - 240W + 56W^2 - 9W^3\right)\Big|_{W_0}^{W} \tag{4.4.3}$$

where W_0 is the initial (ion matrix sheath) value of W. For $W_0 = 0$ (the limit of large P), this function is plotted in Figure 4.13. The acceleration of the sheath as it nears the axis can be clearly seen as an increase in the slope of this curve as it nears W=1. Noting that the sheath reaches the cylinder axis at $\Theta = 0.0936$, Sheridan calculates that $T_{axis} \approx 1.2P$. Although this result and the result plotted in Figure 4.13 are in the large P limit, they are in good agreement with actual values for $P \ge 2$.

As noted at the beginning of this section, the electrons must have somewhere to go as the remaining plasma volume shrinks with the expansion of the sheath. In addition, in a long cylinder, a ground reference must be maintained – something which may be difficult to achieve with a long, thin plasma column. A common experimental way to avoid both these problems is to put an auxiliary electrode on the cylinder axis [34]. The effect of varying the relative radii of the auxiliary electrode and implanted surface has been investigated by Zeng and co-workers [35, 36], who noted that the size chosen must balance two conflicting trends: as the radius of the auxiliary electrode increases, the average implantation energy increases toward the potential applied to the implanted surface, but the implanted dose is reduced due to the smaller volume of initial plasma. It is suggested from the results of particle-in-cell simulations that an auxiliary electrode radius between 0.1 and 0.3 times the radius of the cylinder is a reasonable compromise for many applications.

4.5 Implant Uniformity and Retained Dose

There are several constraints on the size of the expanding sheath formed during PIII. The final sheath width should be small enough that it does not intersect the vacuum chamber walls, which could result in loss of implant uniformity. Similarly, in batch implantation, the sheaths from neighboring workpieces should remain separate. These constraints are considered in more detail in § 6.4.1.

An important issue is sheath conformality around the workpiece. If the sheath is allowed to grow large compared with the features of the component to be implanted, the conformality and resulting uniformity will be compromised. Insight into conformality issues is gained from the computer simulation shown in Figures 4.14 and 4.15, which are from $2\frac{1}{2}$-dimensional (two spatial dimensions, three velocity dimensions) electromagnetic particle-in-cell (PIC) calculations [37] to self-consistently model PIII of two automobile pistons [38, 39]. The piston application is described in § 10.2. The numerical methodology in PIC simulations is that the full set of Maxwell's equations, including displacement currents, is solved at each time step on a regular Eulerian (that is, non-moving) mesh. In these cylindrical (*r,z*) calculations, the radial and axial resolution is 2.0 and 1.5 mm, respectively, which is small compared to the sheath width, *s(t)*, which ranges between 16.5 and 105 mm in this series of calculations. The plasma is modeled by an array of 26,000 electrons and 26,000 $C_2H_2^+$ acetylene ions, which are initially cold with a uniform density n_0 of 2.5×10^{14}, 1.0×10^{15}, or 1.0×10^{16} particles/m^3.

Each workpiece has an outer diameter of 82 mm and length of 50 mm. They are electrically connected to an external voltage supply by a cantilevered rod and surrounded by a 318-mm-diameter concentric vacuum chamber. In Figs. 4.14 and 4.15, the workpieces are located at axial positions z = 62 to 112 mm, and 125 to 175 mm. In the calculation, the voltage has a pulse shape consisting of a 50 ns linear rise followed by a 20 μs flat top. However, results are shown in Figure 4.14 and 4.15 to only 480 ns. Calculations are conducted for a bias voltage of 25 kV, and secondary electron emission (§ 4.3) is neglected.

The calculations yield self-consistently the position of the sheath edge *s(r,z)* as a function of time, with interesting qualitative and quantitative implications. For $n_0 = 10^{16}$ m^{-3}, we find s_o=17 mm which reveals conformality during early times. At 2.5×10^{14} m^{-3}, however, s_o is 105 mm, indicative of poor conformality at all times. For all cases, as the sheath grows, its form changes from an approximately cylindrical to spherical shape, while the ion current decreases consistent with the Child-Langmuir scaling.

Quantitative information extracted from the simulations includes the time-integrated average energy E_i, implanted dose D_i, and mean angle of incidence θ of implanted ions along the surface of the workpiece as a function of time. The plots in Figure 4.15 are for *t*=80, 180, and 480 ns. The time *t*= 80 ns corresponds to a time shortly after the ion matrix phase has been established. Relatively few low-energy ($E_i \le 7$ keV) ions have reached the workpiece by this time, especially for low n_0. By *t*=180 ns, the ion matrix is becoming depleted for low n_0, but has not yet reached the Child-Langmuir equilibrium. Integrated ion energies rise to $E_i \le 14$ keV, though this value still includes contributions from the early-time, low-energy ions. By *t*=480 ns, the ion matrix has been depleted in all cases, Child-Langmuir flow has begun, and E_i rises to $\le$ 19.5 keV. This cannot be directly correlated to the snapshot of the particle distributions in Fig. 4.14, since ion transit times are comparable to this time. At *t*= 480 ns, the instantaneous flux is characterized by energies of 22.7-23.2 keV. E_i does not correspond to the full bias voltage because of the finite expansion of the sheath during one transit time (§ 4.2.3.4). The time elapsed between ion entry into the sheath edge and implantation into the object is of order ω_{pi}^{-1}, i.e. about 450-500 ns for the $n_0 = 10^{15}$ m^{-3} case. As ions accelerate through the potential well, the well changes both in magnitude and shape. Average ion energy therefore changes as one scans along the surface of the

object. As the plasma density is increased, so does the dose at any given elapsed time. The increase in dose scales less than linearly with n_0. Finally, we note that higher n_0 leads to ion flow incidence which is close to normal to the surface. At later times, the differences begin to relax. This situation is roughly what we expect, based upon the higher degree of conformality which is seen for high density calculations. Much later in time, as all sheaths lose conformality, we expect this difference to be diminished.

The dose D_i varies by almost 25% along the surfaces. This is due to what might be termed "spherical convergence." Although the exact details depend on the geometry of the implanted object, much of this effect results from intersecting a spherically converging flow with a cylindrical object. While it does not account for the exact dose pattern, it is useful and generic in understanding dose distributions in long cylindrical arrays of objects. It should be noted, however, that the high density "spikes" at corners of the workpieces are mostly numerical artifacts. At a corner, the numerical diagnostic "counts" all ions entering a cell, not just those crossing the outer surface. The retained dose D_r is a more relevant parameter for characterizing implantation than total absorbed dose. D_r depends upon both E_i and θ, the angle from normal. Implant depth profiles are plotted as function of θ in Fig 4.16(a). The profile and retained dose are estimated with the *Profile*™ Code [40] for $D_i = 2 \times 10^{17}$ cm^{-2}, $E_i = 12$ keV implants of carbon into aluminum. Lower D_r is observed as θ increases in Fig. 4.16(b), because less of the ion's energy is directed normal to the surface (resulting in a shallower implant), and increased sputtering produces faster surface recession, removing some already implanted ions (§ 3.1.8).

A final point about the electron and ion distributions in Fig. 4.14 should be noted. Large “holes” can be seen at the axial end-faces at later times. These evacuated regions reflect that all of the initial plasma in our numerical chamber has been exhausted. In a physical chamber with the same dimensions, the same phenomenon will occur. Increasing the axial length of the chamber will delay the onset of plasma exhaustion. Simple estimates indicate that a sufficiently long voltage pulse can lead to complete plasma usage even in large PIII chambers. Addressing this issue quantitatively requires considerations of the bias voltage and the power of the plasma source. The information presented in § 4.2 and § 6.3 can guide in calculating the appropriate values. The process of plasma exhaustion in small chambers can be a real effect and should be evaluated when designing a PIII process, as discussed in § 6.3.

4.6 Implantation of Non-Conducting Materials

There exist applications for ion implantation into electrically insulating materials (e.g., ceramics, glasses, or polymers). For example, polymers implanted with a wide variety of ions at relatively low doses of 10^{16} cm^{-2} or less show remarkable improvements in surface mechanical, gas permeation, and electrical properties [41, 42]. For some materials (polymeric materials in particular), implantation at high dose levels may produce significant changes in the material’s electrical conductivity as well as changes of its tribological properties.

The PIII process requires a conducting electrode to provide the accelerating electric field to extract ions from the surrounding plasma. When implanting metals, the workpiece itself serves as the electrode. For non-conducting objects, an auxiliary conducting electrode is necessary. One

possible configuration is placement of an electrode behind an insulating workpiece as shown in Fig. 4.17. For this case, the sheath voltage (and hence the implantation energy) will be lowered by two effects: (1) the dielectric voltage drop across the workpiece; and (2) the positive surface charge that accumulates from the ions implanted and secondary electrons emitted during a pulse. While one often assumes that plasma electrons rapidly neutralize the accumulated charge between pulses, this neutralization process has not been studied in detail. Changes in the plasma sheath dynamics and implanted energy spectrum have been modeled by Emmert [43]. He showed that the voltage on the dielectric surface, i.e. the effective implantation voltage, is

$$V_1 = \frac{V_0(t) - \left[n_0\, e\, d\, (s - s_0)/(\varepsilon_0 \kappa)\right]}{1 + \left[4d/(3s\kappa)\right]}, \tag{4.6.1}$$

where $V_0(t)$ is the voltage applied to the underlying conductor, d is the thickness of the dielectric, κ is its dielectric constant, n_0 is the plasma density, s_0 is the plasma sheath thickness before the implantation pulse is applied, and $s=s(t)$ is the thickness of the expanding sheath. Emmert estimates that the reductions in implantation energy and dose in polymer sheets typically range between 10% and 40%, depending on polymer thickness and plasma parameters.

Linder and Cheung [44] found that secondary electron emission from the insulating surface has an even greater influence on surface charging, since the emission of secondary electrons contributes the same charge as implantation of an ion, and the secondary emission coefficient is much greater than unity (§ 4.3).

The reduction in sheath voltage from the dielectric potential drop may be avoided if the workpiece can be placed on a conducting support table and covered with a highly transparent, conducting grid that is electrically connected to the table as illustrated in Figure 4.18 [45]. The

grid is displaced several mm above the surface of the workpiece to eliminate shadowing effects. The grid is constructed from a material that has both a low sputter yield and low secondary electron emission and is sufficiently flexible to conform to the general surface features of the workpiece. When the voltage pulse is applied to the support table, this voltage also develops along the entire grid surface. Because the grid is highly transparent, ions accelerated toward the grid are implanted into the object's surface with the full implantation voltage. During implantation, ions that intercept and impact the metal grid cause secondary electrons to be emitted which neutralize the ions implanted into the non-conducting object. The over-layer grid technique has been successfully used; details are described in § 10.6.

4.7 Implantation at Elevated Temperatures

In PIII the thickness of the modified surface layer is usually limited to the projected ballistic range R_p of energetic ions in solids (§ 3.1.3). For the ion species, energies, and workpiece materials of interest, R_p is relatively shallow, usually 100 nm or less (Fig. 4.19). In many situations, such as mechanical wear, substantially larger depths are required. PIII can be combined with other surface treatment methods, such as thermal nitriding, carburizing, physical vapor deposition, or chemical vapor deposition. With these hybrid techniques, deeper modified surface layers are achieved, with material performance characteristics frequently surpassing those obtained with only one of the processes.

PIII is related to conventional diffusion-based surface modification techniques such as ion nitriding or carburizing [46] in that ions and atoms produced in a plasma are introduced into the

workpiece surface. Traditional ion nitriding and carburizing rely on diffusion and require high substrate temperatures where the diffusion coefficient becomes sufficiently large. Ion nitriding is typically performed at temperatures between 340°C and 565°C, using mixtures of N_2 and H_2 with total pressures of a few hundred Pa, and with accelerating voltages of up to 1000 V. Equilibrium stoichiometric compounds, such as γ-Fe_4N or ε-Fe_3N in steel nitriding, are formed. PIII is similar in that ions such as nitrogen are attracted to a workpiece by an electric field. However, unlike nitriding or carburizing, ion implantation is a kinetic, non-thermal process in which ions are ballistically pumped into the substrate, which can be kept at any temperature. Thus, one can treat low melting temperature materials such as polymers, aluminum, or some heat-treated steels which would loose their temper at the elevated temperatures required for a diffusion process. Other advantages of PIII include the ability to achieve non-equilibrium stoichiometric composition, enabling the production of higher (oversaturated) implant concentrations. This is often associated with improved surface properties such as hardness (§ 10.1), and may be unobtainable by conventional equilibrium thermal methods. In addition, one can avoid the formation of brittle compounds such as γ-Fe_4N, also known as the "white layer," which are common in nitriding.

The modified surface layer obtained by PIII is several orders of magnitude thinner than that of nitriding. PIII at elevated substrate temperature represents an interesting hybrid process combining ion implantation and plasma nitriding [47-51]. By combining nitrogen PIII and diffusion, one creates a hybrid microstructure, consisting of an outermost, non-equilibrium layer typical of traditional ion implantation (either amorphous or crystalline containing in excess of 20 at.% nitrogen) backed by a substantial diffusion zone of much lower nitrogen content. The

bombardment of energetic ions during the PIII process is often found to be an adequate heat source, thereby eliminating the need for auxiliary heating. One may apply additional heating, although often cooling is desired rather than additional heating. Adjusting the workpiece cooling rate and/or average ion implantation current allows one to control the temperature [52]. Greater depths are obtained (0.5 μm at 300°C, and > 10 μm at 500°C), consistent with diffusion. Alloying elements present in steel influence the diffusion depths. Greater depths are observed in steels that contain a high proportion of nitride-forming elements. This hybrid PIII-nitriding process is different than beamline ion implantation at elevated temperature in that additional neutral nitrogen is absorbed by the workpiece. In particular, the significant population of atomic nitrogen and metastable excited N_2 at the workpiece surface in PIII inhibit outward diffusion that occurs with beamline ion implantation at elevated temperatures. Consequently, the PIII-retained dose often exceeds the implanted dose, which is indicative that adsorption of the background high-activity gas and its inward diffusion play an important role.

Because of the high pulsed voltages which are required to obtain significant ion penetration into the workpiece surface (usually many 10 kV for PIII), and the rapid pulse repetition rate provided by modern pulse modulators, significant power loads on the workpiece are possible. Since the externally measured current to the workpiece includes the secondary electron current, the ion current to the workpiece is reduced from the measured total current by the factor $1/(1+\gamma_{SE})$, Eq. (4.3.1). Since γ_{SE} can vary from less than 1 to as much as 20 (see § 4.3), prior knowledge of the expected range in γ_{SE} for a given workpiece implantation process is very valuable in designing the workpiece support and cooling system. A rough estimate of the temperature rise of a workpiece is

$$\Delta T \approx \frac{I_{total} V_p \tau_p f_p t_{impl}}{\left(1+\gamma_{SE}\right) M_t \, c_p}, \tag{4.7.1}$$

where ΔT is the expected temperature rise of the workpiece (K), I_{total} is the ion and secondary electron current (A), V_p is the pulsed voltage applied to the workpiece (V), τ_p is length of each voltage pulse (s), f_p is the pulse repetition rate (s^{-1}), t_{impl} is the total implantation time (s), γ_{SE} is the secondary electron emission coefficient, M_t is the total workpiece mass (kg), and c_p is the workpiece specific heat (J/kg-K). Here it is assumed that the workpiece is thermally isolated from the electrical feedthrough and the vacuum chamber, and that radiative cooling is still negligible. In practice, a workpiece will reach an equilibrium temperature at which thermal energy transport through the electrical connection and mechanical support and radiative energy losses to the vacuum chamber wall match the average ion energy deposition.

A more precise calculation of the workpiece temperature requires solving the heat conduction equation

$$\rho \, c_p \frac{\partial T}{\partial t} = \nabla \cdot k_{th} \nabla T \tag{4.7.2}$$

for the given workpiece and holder geometry, including terms describing radiative heat losses (ρ is the density of the substrate material, and k_{th} is the thermal conductivity in W/(K m)). Approximate analytical solutions for numerous practical cases can be found in text books such those by Holman [53] and Carslaw and Jaeger [54]. Here we present only the simple but relevant example of semi-infinite, one-dimensional solid with a uniform heat flux. The heat conduction equation (4.7.2) reads in the case

$$\rho \, c_p \frac{\partial T}{\partial t} = k_{th} \frac{d^2 T}{dx^2} \tag{4.7.3}$$

where x is the depth under the surface. The boundary condition is

$$-k_{th}\frac{dT}{dx}=Q_h-Q_{rad}-Q_{con} \tag{4.7.4}$$

where Q_h is the power density to the surface (in W/m^2), $Q_{rad}\approx\varepsilon\,\sigma_{SB}\left(T_s^4-T_w^4\right)$ is the radiative cooling with ε the emissivity, σ_{SB} the Stefan-Boltzmann constant, T_s is the local surface temperature, T_w is the chamber wall temperature, and Q_{con} is the heat flux due to conduction. Even in this simple case, the heat conduction equation is nonlinear and analytical solutions exist only for special cases. If radiation and heat conduction cooling can be neglected, the solution is [54]

$$T(x,t)=\frac{2Q_h}{k_{th}}\left[\sqrt{\frac{\kappa\,t}{\pi}}\,\exp\left(-\frac{x^2}{4\,\kappa\,t}\right)-\frac{x}{s}\,\text{erfc}\left(\frac{x}{2\sqrt{\kappa\,t}}\right)\right] \tag{4.7.5}$$

and the substrate surface temperature is obtained for $x=0$

$$T_s=T(0,t)=\frac{2Q_h}{k_{th}}\sqrt{\frac{\kappa\,t}{\pi}} \tag{4.7.6}$$

where $\kappa=k_{th}/\left(\rho\,c_p\right)$ is the thermal diffusivity (in m^2/s).

Depending on the workpiece geometry, desired treatment areas, workpiece support details, and temperature sensitivity of the workpiece, it is quite possible that the pulser repetition rate may have to be reduced to prevent overheating of the workpiece. An example of such a case involves the implantation of a long, thin, solid rod of material for which both ends of the rod must be implanted. Since the rod is supported (and cooled) only at one end, a temperature gradient will develop along the length of the rod during implantation according to the rate of energy deposition on the surface (which tends to be concentrated at the rod tip by the action of the

plasma sheath). If the power flux to the rod is sufficiently large, the rod tip will exceed the maximum allowed temperature.

If the workpiece and mechanical support are thermally isolated from the vacuum chamber, and no active cooling is employed, the ion energy deposition may be used to intentionally heat the workpiece. For this type of operation, it is possible to control the workpiece temperature by means of varying the pulser repetition rate based on a measurement of the workpiece temperature. This measurement may be done by IR pyrometry, or suitably applied thermocouples, or other techniques. Again, the issues of thermal transport within the workpiece and secondary electron emission are important considerations for temperature uniformity and heating rate of the workpiece.

The power applied to the workpiece in this fashion is relatively expensive because the power source is the high voltage pulser, a relatively complex system. Workpieces which can tolerate temperatures high enough for enhanced thermal diffusion of the implanted species are most likely suitable for other modification techniques such as thermal or plasma assisted thermal nitriding or carburization. Therefore, elevated-temperature-PIII performed in this way will probably find industrial applications for selected materials and treatment processes only.

4.8 Plasma Immersion Ion Implantation with Deposition

4.8.1 Introduction

The possibilities of Plasma Immersion Ion Implantation (PIII) are greatly extended when film formation is added to the ion implantation process. Various methods of film formation can be applied such as physical vapor deposition (evaporation, sputtering), chemical vapor deposition (including deposition from metallorganic gases), and cathodic arc plasma deposition. PIII *with deposition* is a hybrid technique which includes deposition and implantation phases. Often the term Plasma Immersion Ion Implantation *and Deposition* (PIIID) is used. In the literature, one may also find other acronyms such as MePIIID for Metal Plasma Immersion Ion Implantation and Deposition, PIIP for Plasma Immersion Ion Processing, and PIID for Plasma Immersion Ion Deposition. A compilation of acronyms can be found in Appendix C.

First attempts of combining PIII with film deposition were made by alternating PIII with sputter deposition [55]. In this work, stainless steel was alternately coated with Ti and implanted with nitrogen by PIII. A similar approach was tested for the formation of various niobium oxide phases (magnetron sputtering followed by oxygen PIII) [56]. In these cases, films were treated with gaseous PIII; no metal plasma was used to modify the coatings.

A combination of reactive magnetron sputtering and PIII was proposed in 1992 for the deposition of nitrides, metal carbides and metal carbo-nitrides [57]. The metal originated from sputter targets and was present throughout the chamber by diffusion in the gas plasma, thus allowing the processing of three-dimensional substrates.

Brown and co-workers [58, 59] were the first to combine PIII with cathodic arc deposition. They used the metal ions for both ion implantation (high bias voltage on) and ion deposition (bias voltage off); the need for a processing gas was eliminated.

In the following sections, various versions of PIIID are discussed. Emphasis is put on PIIID using metal plasmas produced by cathodic arcs because cathodic arc plasmas are fully ionized and therefore of particular importance to PIIID. Any solid sufficiently conducting that it can serve as an arc cathode can be transformed into the plasma state, that is: metals, metal alloys, semi-metals (e.g., carbon in its graphite phase) and semiconductors such as highly doped or heated silicon, germanium, and boron.

PIIID techniques producing amorphous hard carbon films are of great practical interest (§ 10). We will discuss the formation of hydrogenated "diamond-like carbon" (DLC, or a-C:H) as well as hydrogen-free, highly tetrahedrally bonded, amorphous carbon, also known as a-C, or ta-C, or "amorphous diamond" (a-D). Conventionally, we will use the acronym "DLC" for the hydrogenated material, and the symbol "a-C" for the non-hydrogenated material.

4.8.2 Plasma Immersion Ion Implantation and Deposition with Cathodic Arc Plasmas

4.8.2.1 Some Peculiarities of Cathodic Arc Plasmas

Cathodic arc plasmas belong to the group of condensable plasmas, that is, a surface coating is generally obtained when using cathodic arc plasmas for PIII&D. The plasma necessary for current transport between the electrodes is formed at micron-size, rapidly moving spots on the

cathode surface. Therefore, plasma ions are made from the *cathode* material. Ions are accelerated by the combined forces of the pressure gradient, local electric fields, and electron-ion friction [60, 61]. Like most cathodic arc processes, ion acceleration happens almost exclusively in the vicinity of the spot. The final ion velocity [62] is $v_i = 1 - 2 \times 10^4 \text{ m / s}$, and is nearly independent of mass and charge state. Ions are supersonic because the ion sound speed

$$v_s = \left(\frac{kT_e + \gamma \; kT_i}{M_i} \right)^{1/2} \approx 2 \left(\frac{kT}{M_i} \right)^{1/2} \qquad (4.8.1)$$

is smaller than v_i. For example, $v_s \approx 4 \times 10^3 \text{ m / s}$ for a copper plasma with $T_e = T_i = T = 3 \text{ eV}$. In (4.8.1), k is the Boltzmann constant, T is the temperature in Kelvin (1 eV corresponds to 11,600 K), M denotes the ion mass, and m_e is the electron mass. The ratio of specific heats, γ, is about 3. The fact that $v_s < v_i$ is an interesting feature that is important because it influences the flux of ions entering the sheath. Another important feature of cathodic arc plasmas is that in contrast to most gaseous plasmas, they are almost always fully ionized and have a mean ion charge state greater than 1^+.

4.8.2.2 Removal of Macroparticles From Cathodic Arc Plasmas

An inherent feature of vacuum arc cathode spots is that liquid droplets (solid particles in the case of carbon) are formed in addition to plasma [63-66]. These droplets are of size 0.1 - 10 µm and are often called “macroparticles” to emphasize their massive nature compared to plasma particles (ions, atoms, and electrons). Macroparticles are not acceptable for a number of applications, and “cleaning” methods are required. The most common approach to separating plasma and

macroparticles is the use of a curved magnetic filter. Details of filtering are discussed in the section on cathodic arc plasma sources and filters, § 7.8.4.

4.8.2.3 Approaches To Plasma Immersion Ion Implantation and Deposition with Cathodic Arc Plasmas

Brown and co-workers [16, 59] reported on a novel surface modification technique by combining PIII and cathodic arc deposition. They demonstrated the method in a number of ways: yttrium ions were implanted into silicon by pulse-biasing the substrate, a titanium-yttrium multilayer structure with atomic mixing at chosen interfaces using two (unfiltered) cathodic arc plasma sources was made, and a thin film of Al_2O_3 was synthesized with a broad, graded interface with the underlying steel substrate. Cathodic arcs were pulsed, and each arc pulse was synchronized with a substrate bias pulse, Fig. 4.20 (a) and (b). Implantation and deposition phases are determined by the presence or absence of the high voltage substrate bias. Since the bias pulses (-30 kV, 1 μs) were shorter than the arc pulses (2 μs), films were formed which were bonded to the substrate through an atomically mixed zone.

In Brown's early experiments, each arc pulse was synchronized with a single bias pulse. The overall efficiency of PIIID can be drastically increased by using long arc pulses (or even DC arc operation), with CW or gated bursts of bias pulses [67] as indicated in Figs. 4.21 (a) and (b). The ratio of ion implantation to deposition is here determined by the duty cycle of the bias voltage (see § 4.8.3).

Wood and co-workers [18] extended the bias pulses for the whole duration of the arc pulses (20 μs) thus achieving pure ion implantation (without film deposition). They tested this concept by implanting erbium into various substrates at an applied voltage of -20 kV.

Sroda *et al.* [68] used a short-pulse filtered cathodic arc system combined with DC-substrate-bias, i.e., only the plasma production by the arc was pulsed (Fig. 4.22 (a) and (b)). Since the filtered cathodic arc plasma flow is fully ionized, all particles (aluminum ions in this case) are accelerated in the sheath between plasma and substrate. In this way, plating-free aluminum ion implantation into silicon was obtained. This concept was later applied to dope *p*-type $\langle 100 \rangle$ Si with antimony [69].

4.8.2.4 Peculiarities of PIIID When Using Cathodic Arc Plasmas

As well as their condensability, vacuum arc plasmas have some other peculiarities: (i) multiply charged ions are present; (ii) vacuum arc cathode spots are prolific producers of fully ionized plasma; (iii) the plasma flow velocity is supersonic with respect to the ion sound speed. These peculiarities lead to some interesting consequences.

<u>Consequences of (i)</u>: The presence of several ion charge states gives rise to several ion energies,

$$E_Z = \left|ZV_b\right| + E_0 \qquad (4.8.2)$$

where E_0 is the ion energy corresponding to the flow velocity, $E_0 = Mv_0^2/2$, and V_b is the applied negative bias voltage. Ions crossing the full sheath width without collisions acquire the discrete energies (depending on their charge state Z, Table 4.6), given by Eq. (4.8.2). This

simplest case corresponds to the collisionless model discussed in § 4.2.2. The extensions of the collisionless model apply accordingly.

The various ion energies lead to various sputter rates; an average sputter rate can be defined as

$$\bar{\gamma} = \sum_{Z=1}^{Z_{max}} \gamma_Z(E_Z) n_Z \bigg/ \sum_{Z=1}^{Z_{max}} n_Z \tag{4.8.3}$$

where $\gamma_Z(E_Z)$ is the energy-dependent sputter rate of Z-fold charged ions, and the densities n_Z represent weight factors determined by the abundance of the Z-fold charged ions in the plasma. The thickness of the ion matrix sheath is given by

$$s_0 = \left(\frac{2\varepsilon_0 |V_b|}{\bar{Z} e n_i} \right)^{1/2}, \tag{4.8.4}$$

and thus it is slightly thinner than s_0 of "standard" gaseous PIII, Eq.(4.2.3), namely by the factor $\bar{Z}^{-1/2}$, where $\bar{Z}$ is the mean ion charge,

$$\bar{Z} = \sum_{Z=1}^{Z_{max}} Z n_Z \bigg/ \sum_{Z=1}^{Z_{max}} n_Z . \tag{4.8.5}$$

and n_i denotes the total ion density (all charge states) at the plasma-sheath boundary. Similarly, the ion plasma frequency is enhanced by a factor $\bar{Z}$.

Consequences of (ii): The plasma density, $n = n_e = \bar{Z} n_i$, is relatively high and the inverse electron and ion plasma frequencies are shorter than typical pulse rise and fall times. The ion fluxes and related ion current densities and deposition rates are high compared to other implantation and deposition techniques. High plasma densities cause the sheath to be very thin, and thus the bias potential drop is concentrated across a short distance. This may lead to breakdown of the sheath, also known as unwanted "arcing" of the substrate.

Consequences of (iii): In the simple sheath models described in § 4.2 (with the exception of the model of Lieberman [7]), it is assumed that the ion current is derived from the number of ions uncovered by the expanding sheath. It has been pointed out that ions enter a subsonic sheath with a non-zero velocity that allows a finite, *stationary* sheath to exist with non-zero ion current [70, 71]. The ion velocity is due to acceleration in the presheath and equals at least the ion sound speed in the stationary case (Bohm criterion [72]). Because the ions of a vacuum arc have already a supersonic speed, the equation for the sheath thickness reads

$$j_i = \overline{Z}\, e\, n_i \left(\frac{ds}{dt} + \mathrm{v_i} \right) \qquad (4.8.6)$$

A simple estimate shows that the ion current at the beginning of a high voltage pulse is dominated by the ds/dt term. For longer bias pulses, the sheath becomes stationary and the ion current is only determined by the second term of Eq. (4.8.6). Since ions have already supersonic speed the need for a presheath has vanished, and thus a presheath may not exist. This issue is the subject of ongoing research.

Equation (4.8.6) is true when the plasma flow is normal to the substrate area. For the side faces of a three-dimensional substrate, the ion flux becomes different in the deposition and implantation phases. A wake is formed downstream from the substrate. A sheath thickness greater than the characteristic dimension of the substrate is required if ion implantation into a three-dimensional substrate with the flowing plasmas is performed. Otherwise, the wake side will have a very low dose. The large sheath thickness can be obtained by choosing a low plasma density combined with a high bias voltage. A relatively uniform implantation of aluminum ions into all faces of a $(2\ \mathrm{cm})^3$ cube was achieved in this way [68]. Generally is it anticipated that

future three-dimensional PIIID with cathodic arcs plasmas will operate with several plasma sources which are placed at well-chosen locations around the workpiece to mitigate the directionality of plasma fluxes.

4.8.3 Sacrificial Layers

A unique feature of ion implantation is that the concentration of species implanted in the substrate material can exceed the limits given by equilibrium thermodynamics. However, the retained dose of implanted ions is limited by sputtering as described in § 4.5. Clapham and co-workers [73] used a thin carbon coating (a "sacrificial layer") on the substrate to increase the retained dose of iodine ions implanted into copper. The idea of a "sacrificial layer" is to protect the original surface of the substrate by a very thin coating. Sputtering is not avoided, but it is the sacrificial layer that is sputtered. Carbon was chosen because its sputtering rate is relatively small due to its small atomic density and nuclear stopping power. The sacrificial layer was deposited prior to ion implantation. Its thickness had to be carefully chosen: if it is too thin then it will be sputtered away before the implantation is finished, and if it is too thick then the incident ions stop in the layer rather than in the underlying substrate. Another drawback is ion mixing of carbon with the substrate due to recoil collisions, which may not be tolerable in some applications.

Rybachikov *et al.* [74] and Tolopa [75] have used vacuum arc metal ion beam sources which can operate alternately in an ion deposition and ion implantation mode by switching the ion extraction voltage. This approach uses "native" sacrificial species.

PIIID offers *in-situ* deposition of sacrificial layers. For instance, by carefully choosing the bias pulse duty cycle for given ion implantation energy and material, the removal of material by sputtering (bias on) can be matched by deposition (bias off). Sputtered atoms are lost from the surface, and thus the sacrificial layer can be kept very thin (a few monolayers) if "repair" is done along with ion implantation. PIIID can be tailored as an elegant *in-situ* "repair" of the sacrificial layer [76].

Deposition and sputtering have to be balanced to obtain a sustainable repair of the sacrificial layer. This can be done by operating at a suitable bias duty cycle which can be defined as

$$\delta = \tau_p \big/ \left(\tau_p + \tau_{off}\right) \tag{4.8.7}$$

where τ_p is the duration of individual bias pulses and τ_{off} is the time between two pulses. If the duty cycle is too low, a film grows on the substrate; if the duty cycle is too high, the substrate including the previously implanted ions will be sputtered. The balance equation can be written as

$$\left(J_i\ \xi_i + J_0\ \xi_0\right)\tau_{off} = \left(\alpha\ J_i\ \left(\gamma_i + p\right) - J_0\ \xi_0\right)\tau_p \tag{4.8.8}$$

where J_i and J_0 are the ion and neutral particle flux density incident upon the substrate, respectively, ξ_i and ξ_0 are the ion and neutral sticking coefficients, γ_i is the actual material and ion-energy-dependent partial sputter rate of previously deposited and implanted ions ("actual" refers here to the rate during a pulse), α is the fraction of the implanted material at the surface, $0 \le \alpha \le 1$, and p is a function proportional to the probability with which a deposited metal ion suffers a knock-on collision (recoil implantation). Some simplifying assumptions have been made in the derivation of (4.8.8): (i) the incident flux is independent of the bias pulse duration, and (ii) the term "pulse duration" is well-defined, assuming short bias rise and fall times.

Equation (4.8.8) can be further simplified since vacuum arc metal plasmas are used which are fully ionized, thus $J_0 = 0$. Then, (4.8.7) and (4.8.8) give

$$\delta = \left(1 + \frac{\alpha}{\xi_i}(\gamma_i + p)\right)^{-1} \qquad (4.8.9)$$

This equation gives the bias duty cycle that should be used to obtain maintained repair of the sacrificial layer. For very rough estimates one may use $\delta \approx (1 + \gamma_i)^{-1}$. Since there is no sacrificial layer at the beginning of the process, sputtering would start with substrate material only. This suggests operating at a variable duty cycle: A sacrificial layer should be deposited at the beginning of the process, i.e. the bias duty cycle should be zero until a thin film has been formed, the thickness of which must be thick enough to cover the substrate but thin enough that energetic ions can be implanted through the film. Once the sacrificial layer is formed, bias pulses can be applied to begin implantation. The duty cycle of the implantation-deposition process can be matched to rebuild the sputtered film after each implantation pulse. In addition to direct implantation, recoil implantation will occur. If desired, the sacrificial layer can be at least partially removed at the end of the implantation process, for instance by simply enhancing the duty cycle.

The relation between implantation and deposition can be illustrated by dynamic Monte Carlo simulations [76]. A dynamic code such as T-DYN 4.0, [77], takes into account gradual changes of the substrate such as composition and layer thickness alterations due to ion bombardment (in contrast to the better-known standard TRIM code, see [78] and § 3.1.10 of this book).

As an example, the implantation of tungsten ions into silicon was studied. The total dose (including deposition) was in the range 5×10^{16} to 2×10^{17} ions / cm^2. The ion energy was 75 keV in the implantation phase, corresponding to a bias voltage of 25 kV (mean ion charge state of vacuum-arc-produced tungsten is 3+). Figure 4.23 shows the tungsten depth profile for various bias duty cycles at a constant dose of 2×10^{17} ions / cm^2. 100% duty cycle corresponds to pure ion implantation without deposition of a sacrificial layer. The retained dose of tungsten is clearly limited by sputtering. A smaller duty cycle (increasing deposition) leads to an increase of the retained dose. When the duty cycle becomes smaller than 10%, a layer starts to grow. Figure 4.24 shows implantation profiles for a constant duty cycle of 50% as a function of dose. The profile reaches its steady-state shape at a dose of 1.5×10^{17} ions / cm^2. By combining ion implantation and thin film deposition, non-equilibrium layers of arbitrarily high dopant concentration and arbitrary thickness can be obtained; the synthesis of otherwise unattainable ion implantation profiles has been dubbed "pseudoimplantation" by Brown *et al.* [79] for a PIIID system using cathodic arc plasmas. Recently, Bender *et al.* [80] came independently to similar conclusions using a PIIID system with an inductively coupled RF plasmas source and neutral vapor deposition.

4.8.4 Ion Mixing and Layer Adhesion

The implantation and deposition phases are alternated in the PIIID technique so as to bombard the freshly deposited film with energetic ions. Both direct and recoil implantation are therefore characteristic of PIIID, leading to the formation of an intermixed layer between substrate and film as can be clearly seen in the examples shown in Figs. 4.23 and 4.24. In contrast to most

other deposition techniques, a PIIID-formed film always has an intermixed layer, the thickness of which depends mainly on the ion energy (bias voltage). Ion induced mixing relieves the stress at the film-substrate interface associated with structural mismatch of substrate and film material (§ 3.2.3). This is one reason why PIIID-formed films often show superior adhesion. Another reason is the cleaning effect of energetic ion bombardment (sputtering), i.e. removal of contaminants from the substrate surface. For instance, water and residual hydrocarbons are removed by energetic ions (bias on), immediately followed by deposition of material (bias off). The removal of contaminants influences the existence and nature of chemical bonds formed between the substrate material and ions deposited. For instance, if working with a carbon plasma, carbide-forming materials such as silicon are excellent substrates. More details about adhesion and stress are discussed in chapters 3 and 10.

As the film grows, an increasing fraction of ions is implanted not only into the original substrate but also into the growing film. To enhance the effect of intermixing but reduce sputtering of the freshly deposited layer, PIIID can be started with high substrate bias pulses and, after an intermixed layer has been formed, continued with low bias. When the growing film becomes thicker than the implantation depth, ion implantation does not contribute any longer to intermixing but may essentially influence the structure of the film.

Ion mixing was already observed in the early experiments by Brown [16, 58, 59]. The formation of an intermixed Ti/Si layer was studied in a similar experiment with a filtered cathodic arc source [81].

4.8.5 PIIID with Multi-Element Metal Plasmas

Cathodic arcs can operate with alloy cathodes thus producing multi-element metal plasmas. The plasma composition is often close to but not identical to the composition of the cathode [82, 83]. Alternatively, multi-element films and multilayers can be formed using two or more filtered cathodic arc sources simultaneously (§ 10.4). Yet another technical approach is to utilize two or more cathodes in a single cathodic arc plasma source [84, 85].

4.8.6 PIIID in the Presence of Reactive Gases

The PIIID technique can be considerably extended by operating the cathodic arc in a reactive gas such as nitrogen or oxygen, as opposed to vacuum operation. Metal ions collide with the gas molecules in transit from the cathodic arc plasma source to the substrate, and the gas becomes partially ionized. At relatively low pressure, metal and gas react preferentially on the substrate surface. It has been found that compound films can easily be formed when operating the cathodic arc source in pulsed mode because the material deposited on the substrate by one arc pulse is subject to bombardment by gas particles before the next arc plasma arrives. In contrast to sputtering, cathodic-arc plasma deposition allows the formation of stoichiometric compound films over a wide range of chamber pressure. Details are discussed in § 10.4.5.

4.9 Electrical System Requirements

Technical power requirements of the vacuum chamber system are discussed in Chapter 6, of plasma sources in Chapter 7, and of the bias pulse modulator in Chapter 8. Here we cover some basic considerations of the PIII&D process only.

The pulsed high-voltage power modulator must be capable of driving the load impedance presented by the workpiece immersed in the surrounding plasma. The dynamic workpiece impedance is determined at early times in the voltage pulse by the characteristics of the rapidly expanding sheath (electron motion away from the workpiece, and collection of increasingly energetic ions by the workpiece). The quasi-steady-state portion of the required workpiece current is represented, in part, by the space-charge limited current density given by Eq. (4.2.1). In addition, allowance must be made for the current component arising from the secondary electrons generated by the ions impacting the surface (§ 4.3). During the quasi-steady, space-charge limited current phase, the plasma acts as a resistive load to the high-voltage pulsed power supply. This electrical resistance R_{pl} of the plasma for a planar sheath is obtained by combining (4.2.1) with Ohm's law, $R_{pl} = V / I_{total}$,

$$R_{pl} = \frac{9}{4\varepsilon_o} \frac{s^2}{A\,(\gamma_{SE}+1)} \sqrt{\frac{M}{2eV}}, \qquad (4.9.1)$$

where A is the workpiece area, and γ_{SE} is the secondary electron emission coefficient. In many applications of interest such as the implantation of large industrial dies, or large arrays of small components, R_{pl} can be quite small. For example, in a 50 kV N^+ implant with s=10 mm, A= 5 m^2 and γ_{SE}=7, the plasma sheath resistance is $R_{pl} = 0.76\,\Omega$. This corresponds to a total pulsed current of 65 kA, provided the pulse modulator is capable of delivering this current! As discussed in Chapter 8, most pulse modulators are incapable of driving this load, so users are

often forced to compromise by implanting with larger sheath width (corresponding to a lower plasma density), or by restricting the workpiece area.

An example of the dynamic resistance can be obtained by the quotient of the time-dependent voltage and current waveforms predicted by a model of PIII [8] shown in Figure 4.25. The time dependent resistance changes drastically throughout the first 10 μs of the pulse. The initial high resistance is due to the low secondary electron coefficient for low energy ions implanted during the pulse rise time, and the model's assumption that a quasistatic Child Law sheath is formed instantaneously. For comparison, experimentally determined voltage, current, and dynamic resistance waveforms are shown in Figure 4.26. The workpiece in this case has an area of ~ 0.13 m^2, and is immersed in a hydrocarbon plasma at a density of $n_0 \approx 6 \times 10^{14}$ m^{-3}.

The ability of the modulator to drive a current corresponding to R_{pl} largely determines the energy spectrum of ions and the therefore the quality of the implant. One figure of merit for a modulator is the rise time of the voltage waveform under load. A large ion current is collected during the initial phase of the high-voltage pulse when the sheath is expanding at a high rate. If the rise time of the voltage is slow (typically anything more than several μs), the ions collected at early times will be of low energy and cause excess sputtering and a lower retained dose (the energy-dependent sputtering rate has a maximum, see § 3.1.8). PIII is an inherently non-monoenergetic implantation process. A voltage pulse with a very short (or even zero) rise time will still produce a significant spread in the energy spectrum of the ions impacting the workpiece, due to implantation of ions initially in the ion matrix sheath, as was discussed in § 4.2.2.2. This energy spectrum spread can be beneficial for tribological applications in that the implanted dose profile

has a fairly flat top, increasing the thickness of the surface layer which has been implanted to almost the peak concentration. This broader, relatively flat profile will increase the amount of time for which the highest concentration of implanted ions is exposed during the wear process. However, the lowest-energy ions also cause significant sputtering, which can reduce the sputter-limited retained dose.

Another figure of merit (although much less critical) is the voltage fall time under load. Again, the important issue is increased sputtering produced by the low energy fraction of incoming ions. Since the ion current is much lower during the voltage fall than during the rise (the sheath region is depleted of its initial ion population), voltage fall times can be significantly longer than rise times without adverse affects.

Since actual processing of workpiece components for tribological applications typically requires a final retained dose in the 10^{17} ions/cm^2 range, a very large number of pulses is required to treat the workpiece surface. As overall treatment time is also an important criterion, it is desirable to apply these pulses as rapidly as practical. Even though the individual pulses are short (a few µs to a few 10s of µs) high pulse repetition rates (hundreds of pps to several thousand pps) lead to significant average power requirements for an operating system. For the example cited above (a 50 kV N^+ implant with s=10 mm, A= 5 m^2 and γ_{SE}=7), operation with 20 µs pulses at a repetition rate of 100 pps would require an average modulator current of almost 130 A, and a supply current (480 V, 3 phases) of over 10 kA. Although this would produce an incident dose on the workpiece of 5×10^{17} cm^{-2} in only 4 minutes, these high current and power levels are not sustainable with normally available facility utilities. By reducing the repetition rate to 3 pps, the

average high voltage current required would be reduced to ~4 A, the 3-phase AC current required would be reduced to 312 A, and the same incident dose would be obtained in 2.3 hours. The pulse current required by the workpiece for these conditions, however, remains at the 64 kA level, which is beyond the capabilities of available modulators. With available modulator technology (Chapter 8), pulse currents from several hundred amperes up to a few kiloamperes are possible. If a modulator capable of supplying 200 A of pulsed current is available, the plasma density surrounding the workpiece must be reduced so that the required workpiece current is within this limitation, otherwise the pulse rise time will be excessive. This reduction in the plasma density would result in an increase in the sheath dimension to approximately 180 mm. For these conditions, however, the modulator repetition rate could be increased dramatically, so that the total processing time required to achieve the desired incident dose would remain close to 2 hours.

Figure Captions

Fig. 4.1 The plasma immersion ion implantation (PIII) process.

Fig. 4.2 (a)-(d). Qualitative behavior of the transient sheath.

Fig. 4.3 Sheath width calculated from Eqs. (4.2.4), (4.2.5) for planar, (4.2.7) – (4.2.11) cylindrical, and (4.2.12) - (4.2.16) spherical geometry, compared with results from the PIC simulation code PDP1 (planar), PDC1 (cylindrical), and PDS1 (spherical) [6]. The results are calculated for a –40 kV implant with zero rise time implant of an object (of radius $r_0 = 5\,\mathrm{cm}$ for the cylindrical and spherical case) immersed into an argon plasma of $n_0 = 3\times10^{14}\,\mathrm{m}^{-3}$ and $T_e = 1\,\mathrm{eV}$.

Fig. 4.4 Implant current density from several models, compared with PIC simulation results for a planar geometry 50 kV nitrogen ion implantation with a 1 μs rise time and a plasma of 4×10^{14} m^{-3} density. The PIC simulation result is from the PDP1 code [6]. The models are: zero-rise time model [2] (§ 4.2.1), ion matrix sheath depletion model [7] (§ 4.2.2.2); finite rise and fall time model [8] (§ 4.2.2.3).

Fig. 4.5 Experimental workpiece current for a 20 μs erbium vacuum arc pulse directed at a 300 cm^2 aluminum workpiece placed 28 cm from the arc, with the 20 μs bias pulse delayed with respect to the vacuum arc pulse.

Fig. 4.6 (a)-(c). Ion density profiles at 1 μs intervals; (a) covers the first 10 μs voltage pulse; (b) covers the 20 μs of off time between pulses; (c) covers the second 10 μs pulse.

Fig. 4.7 Sheath position vs. time for three 10 μs voltage pulses separated by 20 μs.

Fig. 4.8 Ion implant current for the three pulses shown in Figure 4.7.

Fig. 4.9 Time required to fill in the depleted region to 95% of the undisturbed plasma density, as a function of sheath width, s, for T_e=1 eV and several values of T_i.

Fig. 4.10 A technique used to suppress secondary electron X-ray generation developed at Hughes Research Company.

Fig. 4.11 A technique for suppressing secondary electrons by trapping them in a transverse B-field to form a virtual cathode layer near the workpiece surface where the local electric field is substantially reduced.

Fig. 4.12 Maximum ion impact energy $u^2_{P,max}$ versus the normalized bore radius P, from equation (4.4.2).

Fig. 4.13 The normalized sheath width W plotted versus the normalized time Θ for a zero-rise time pulse, as defined by equation (4.4.3).

Fig. 4.14 Particle-in-cell (PIC) simulations of PIII into two automotive pistons for initial plasma $C_2H_2^+$ densities n_0 of (a) 2.5×10^{14}, (b) 1.0×10^{15}, and (c) 1.0×10^{16} ions m^{-3}. Positions of electrons and ions are plotted for times t = 80, 180, and 480 ns into the PIII pulse.

Fig. 4.15 Time-integrated average energy E, implanted dose D_i and mean angle of incidence θ of implanted ions along the outer surface of the pistons for initial plasma $C_2H_2^+$ densities n_0 of (a) 2.5×10^{14}, (b) 1.0×10^{15}, and (c) 1.0×10^{16} ions m^{-3} at times t = 80, 180, and 480 ns. The workpieces are located at axial positions z = 6.2-11.2 cm and z = 12.5-17.5 cm.

Fig. 4.16 (a) Computed profiles for $D_i = 2\times10^{17}$ cm^{-2} implant of 12 keV carbon into aluminum with angle of incidence θ = 0, 20, 40, and 60°; (b) Retained dose D_r as a function of θ.

Fig. 4.17 PIII into insulating dielectric workpiece with a conducting metallic electrode substrate.

Fig. 4.18 PIII into a insulating workpiece with a conducting highly transparent mesh electrode (courtesy of Hughes Research Laboratory).

Fig. 4.19 Predicted ballistic range of a variety of ions into steel and aluminum, versus implantation energy.

Fig. 4.20 (a) Schematic of the arrangement of early PIIID experiments; (b) sequences of arc and bias pulsing, after [16, 59].

Fig. 4.21 (a) PIIID with long arc pulses and gated bias pulses; (b) sequences of arc and bias pulsing, after [67].

Fig. 4.22 (a) Arrangement for metal ion implantation without film deposition; (b) sequences of arc and bias pulsing, after [68].

Fig. 4.23 Monte-Carlo simulation of tungsten PIIID (75 keV, 2×10^{17} ions / cm^2) into silicon as a function of bias duty cycle, after [86].

Fig. 4.24 Monte-Carlo simulation of tungsten PIIID (75 keV, 50% duty cycle) into silicon as a function of dose, after [86].

Fig. 4.25 Dynamic resistance predicted by the model of Stewart and Lieberman [8], for a 40 kV implantation with a 1 μs rise time into a 0.5 m^2 planar workpiece, surrounded by a 10^{15} m^{-3} N_2^+ plasma. A secondary electron emission coefficient of 20 at 40 kV, varying as (implant energy)$^{1/2}$ is assumed.

Fig 4.26 Experimentally determined voltage, current, and dynamic resistance waveforms for implantation of a workpiece of ~0.13 m^2 immersed in a hydrocarbon plasma at a density of ~6×10^{14} m^{-3}.

Tables for Chapter 4

Table 4.1 Advantages and potential limitations of PIII relative to conventional beamline ion implantation.

Advantages	*Limitations*
Non-line-of sight: can treat large, heavy, and complicated shapes	No mass separation
	Minimum feature size ~ sheath width
Process time independent of surface area	Inhomogeneous implant energy distribution
Compatible with traditional plasma enhanced chemical vapor deposition and semiconductor cluster tools	Secondary electrons limits efficiency and generates X-rays
Low temperature process	Limited practical working voltage
Charge build-up in insulating workpieces neutralized by plasma	Accurate in-situ dose monitoring is difficult

Table 4.2 The first 10 coefficients of the expansion for β and α.

n	β	α
1	+1.0	+1.0
2	-0.4	-0.3
3	+0.09166667	+0.075
4	-0.01424242	-0.0143182
5	+0.001679275	+0.00216088
6	-0.0001612219	-0.000267912
7	+0.00001293486	+0.0000284453
8	-8.87693×10^{-7}	-2.68867×10^{-6}
9	$+5.46192 \times 10^{-8}$	$+2.228897 \times 10^{-7}$
10	-2.94843×10^{-9}	-1.69754×10^{-8}

Table 4.3 Measured secondary electron coefficients, γ_{SE}, for **argon** ions on a variety of materials in a PIII experiment (data from [20]).

Material	*Energy*		
	20 keV	30 keV	40 keV
Stainless Steel 304	4.4	5.3	5.4
Copper	4.1	4.5	4.7
Ti-6Al-4V	4.5	4.6	5.2
Graphite	10.3	11.7	-
Aluminum (oxidized)	14.7	16	15.2
Aluminum (etched)	11.1	11.8	12.8

Table 4.4 Measured secondary electron coefficients, γ_{SE}, for **nitrogen** ions on a variety of materials in a PIII experiment (data from [20]).

Material	*Energy*		
	20 keV	30 keV	40 keV
Stainless Steel 304	4.8	6.2	7.3
Copper	3.9	4.9	6.1
Ti-6Al-4V	5.0	6.2	7.7
Graphite	8.6	10.8	-
Aluminum (oxidized)	14.5	18.5	-
Aluminum (etched)	15.8	16.9	19.1

Table 4.5

Reduction of X-ray radiation by using enclosure technique developed at Hughes Research Laboratory.

IMPLANTATION VOLTAGE (kV)	TOTAL CURRENT TO PLASMA (mA)	ENCLOSURE USED? (YES/NO)	DOSIMETER READING (mRAD/hr.)
50	20	NO	20
50	20	YES	<<1 (Could not measure)
75	15	NO	85
75	15	YES	20

Table 4.6

Melting and boiling temperature of cathode materials (data from [87]), mean ion charge state $\bar{Z}$, and ion charge state distributions (CSDs) of vacuum arc plasmas, measured about 100 µs after arc initiation. CSD data represent average over 16 or more individual measurements (data from [13]. Boron data from [88]).

Atomic Number	Symbol	T_{melt} (°C)	T_{boil} (°C)	$\bar{Z}$	1	2	3	4	5	6
3	Li	180.5	1347	1.00	100					
5	B	2300	2550	1.11	89	11				
6	C	3550	4827	1.00	100					
12	Mg	648.8	1090	1.54	46	54				
13	Al	660.4	2467	1.73	38	51	11			
14	Si	1410	2355	1.39	63	35	2			
20	Ca	839	1484	1.93	8	91	1			
21	Sc	1541	2831	1.79	27	67	6			
22	Ti	1660	3287	2.03	11	75	14			
23	V	1890	3380	2.14	8	71	20	1		
24	Cr	1857	2672	2.09	10	68	21	1		
25	Mn	1244	1962	1.53	49	50	1			
26	Fe	1535	2750	1.82	25	68	7			
27	Co	1495	2870	1.73	34	59	7			
28	Ni	1453	2732	1.76	30	64	6			
29	Cu	1083	2567	2.06	16	63	20	1		
30	Zn	419.6	907.0	1.20	80	20				
32	Ge	937.4	2830	1.40	60	40				
38	Sr	769	1384	1.98	2	98				
39	Y	1522	3338	2.28	5	62	33			
40	Zr	1852	4377	2.58	1	47	45	7		
41	Nb	2468	4742	3.00	1	24	51	22	2	
42	Mo	2617	4612	3.06	2	21	49	25	3	
46	Pd	1552	3140	1.88	23	67	9	1		
47	Ag	1410	2355	2.14	13	61	25	1		
48	Cd	320.9	765	1.32	68	32				

49	In	156.6	2080	1.34	66	34				
50	Sn	232	2270	1.53	47	53				
51	Sb	630.7	1750	1.00	100					
56	Ba	725	1640	2.00	0	100				
57	La	921	3457	2.22	1	76	23			
58	Ce	799	3426	2.11	3	83	14			
59	Pr	931	3512	2.25	3	69	28			
60	Nd	1021	3068	2.17	0	83	17			
62	Sm	1077	1791	2.13	2	83	15			
64	Gd	1313	3266	2.20	2	76	22			
66	Dy	1412	2562	2.30	2	66	32			
67	Ho	1474	2695	2.30	2	66	32			
68	Er	1529	2863	2.36	1	63	35	1		
69	Tm	1545	1947	1.96	13	78	9			
70	Yb	819	1194	2.03	3	88	8			
72	Hf	2227	4602	2.89	3	24	51	21	1	
73	Ta	2996	5425	2.93	2	33	38	24	3	
74	W	3410	5660	3.07	2	23	43	26	5	1
77	Ir	2410	4130	2.66	5	37	46	11	1	
78	Pt	1772	3827	2.08	12	69	18	1		
79	Au	1064	2807	2.97	14	75	11			
82	Pb	327	1740	1.64	36	64				
83	Bi	271.3	1560	1.17	83	17				
90	Th	1750	4790	2.88	0	24	64	12		
92	U	1132	3818	3.18	0	12	58	30		

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