Charge fluctuations for particles on a surface exposed to plasma

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Abstract

We develop a stochastic model for the charge fluctuations on a microscopic dust particle resting on a surface exposed to plasma. We find in steady state that the fluctuations are normally distributed with a standard deviation that is proportional to \((CT_e)^{1/2}\), where \(C\) is the particle-surface capacitance and \(T_e\) is the plasma electron temperature. The time for an initially uncharged ensemble of particles to reach the steady state distribution is directly proportional to \(CT_e\).
As features on integrated circuits become smaller, the problem of contamination by microscopic particles becomes larger. The best solution is to minimize particle creation and to prevent particles from reaching the substrate. However, if particles are deposited on the substrate then methods for removing them are needed. One proposed method is called plasma-assisted electrostatic cleaning (PAEC).

PAEC works by exposing a surface with dust particles on it to a plasma (Fig. 1). It is conjectured [1] that a particle can acquire a net charge $Q < 0$ from the fluxes of charged plasma species. The electrostatic force on the particle due to the sheath electric field $E_w$ is $QE_w$. When this force exceeds the adhesive force the particle is pulled from the surface and experiences a large acceleration across the sheath. If there are no nearby regions where particles can be trapped [2, 3], the particle will move away, and the surface will have been “cleaned.” Thus, the plasma serves two purposes: charging the contamination particle and enhancing the electric field at the substrate. Several experiments [1, 4, 5] have shown that plasma exposure can remove micrometer to nanometer-diameter particles from both insulating and conducting surfaces.

Sheridan and Goree [1] coated an aluminum surface with 0.2–10 $\mu$m alumina grains and...
found that significant particle removal occurred in a low-density plasma \( n_e \approx 10^8 \text{cm}^{-3} \) when the surface was exposed to energetic electrons (59 eV) from an emissive filament. They observed that the removal rate increased with plasma density and decayed exponentially with time. Flanagan and Goree \cite{4} used JSC-1 (Johnson Space Center lunar simulant one) particles on a glass substrate, again for low plasma densities and with energetic electrons, and verified that the time constant for removal decreases with increasing plasma density. They found time constants ranging from 30 s to 1 s for plasma densities from \( 2 \times 10^6 \text{cm}^{-3} \) to \( 2 \times 10^8 \text{cm}^{-3} \). Lytle et al. \cite{5} performed experiments using a high density pulsed helicon source to remove particles as small as 30 nm from a dielectric substrate. Their results demonstrate that a minimum plasma exposure time is required for particle removal. In Lytle’s studies the reported electron temperature was low (\( \approx 3 \text{eV} \)), but the plasma density was 3 to 4 orders of magnitude larger than that in the other experiments \cite{1,4}.

The dominant force holding a microscopic particle to a surface is thought to be the London-van der Waals force \cite{6,7}. The adhesive force on 10–100-nm diameter particles is reported \cite{7} to be \( \sim 1–10 \text{nN} \). An estimate for the van der Waals force between a spherical particle of radius \( a \) and a smooth, flat surface is \cite{4} \( F_{\text{vdW}} = H a / (6 h^2) \), where the Hamaker constant \( H \approx 10^{-19} \text{J} \) and \( h \) is the separation between the particle and the surface (Fig. 1). For a characteristic separation \( h = 0.3 \text{nm} \) and radius \( a = 10 \text{nm} \), \( F_{\text{vdW}} \approx 2 \text{nN} \). Flanagan \cite{4} estimated for his experiment that \( E_w \) may have been as large as \( 10 \text{kV/m} \). For this value of \( E_w \) a particle charge \( Q \approx -10^6 \text{e} \) would be required to overcome the predicted adhesive force. There is no evidence that microscopic particles can attain such large charges; the potential of a 10-nm radius particle in free space with this charge would be \( -150 \text{kV} \). Consequently, it seems likely that adhesive forces are significantly overestimated for typical processing surface conditions and that most particles removed by plasma cleaning are loosely bound. This may be due to surface contamination and/or to the fact that most particles are not perfect spheres and so rest on the surface at a small number of contact points whose asperity size is much less than the particle size, giving a reduced effective radius.

One way that a particle on a biased surface can acquire charge is by sharing charge with that surface. Flanagan \cite{4} referred to this as the “shared charge model.” The shared charge on a spherical particle on a flat surface with electric field \( E_w \) is \cite{8} \( Q = (1.64)4\pi\varepsilon_0 E_w a^2 \), where the factor of 1.64 is a small enhancement because the particle is a perturbation to the otherwise flat surface. For microscopic particles under typical plasma conditions, the
shared charge is small. For example, for $E_w = 10$ kV/m and $a = 500$ nm, $Q = -2.9e$. That is, on average, microscopic particles on a surface have $|Q| \lesssim e$ due to shared charge. Such an average charge is much too small to explain plasma assisted cleaning.

Particles can also acquire charge because of electron and ion fluxes from the plasma. In steady state, these fluxes balance. However, fluctuations in the particle charge may be significant due to the discrete nature of the charging process. It is found experimentally \cite{1,4} that the rate of particle release during plasma cleaning decays exponentially, indicating that each particle release is an independent random event. This is consistent with release being due to particle charge fluctuations, where release occurs during large negative excursions in charge. In what follows, we develop a model of charge fluctuations caused by electron and ion fluxes to a particle on a surface.

The ion flux across the sheath edge is $\Gamma_i = n_0 c_s$ (Fig. 1) where $n_0$ is the plasma density at the sheath edge, $c_s = \sqrt{eT_e/m_i}$ is the ion acoustic speed and $T_e$ is the effective electron temperature in eV. We assume a single ion species with charge $+e$, and neglect secondary electron emission. Since the sheath is essentially source-free, continuity requires that $\Gamma_i$ is also the ion flux at the substrate. The frequency with which ions strike a particle on the surface with ion collection area $A_i$ is $\nu_i = \Gamma_i A_i$. The probability that a particle collects an ion in a time interval $\Delta t \ll \nu_i^{-1}$ is then $P_i = \nu_i \Delta t$, which is assumed independent of the particle’s potential.

For electrons in thermal equilibrium (i.e., Boltzmann electrons), the electron flux to a surface at a potential $\phi$ with respect to the sheath edge is

$$\Gamma_e(\phi) = \frac{1}{4} n_0 \bar{v} e^{\phi/T_e},$$

where $\bar{v}$ is the average electron speed. The average frequency with which electrons strike a particle with electron collecting area $A_e$ is then $\nu_e = \Gamma_e A_e$, and the probability of collecting an electron in $\Delta t$ is $P_e(\phi) = \nu_e \Delta t$. In the typical case where $\Gamma_i < \Gamma_e(0)$ the particle will have a steady-state floating potential $\phi_f < 0$ such that the electron and ion collection rates are, on average, equal. Assuming equal collection areas, $A_i = A_e$, $\phi_f$ is a solution of $\nu_i = \nu_e(\phi_f)$.

Now consider a fluctuation around the floating potential, where the particle and surface are assumed to have the same average $\phi_f$. The particle’s potential can be written as $\phi = \phi_f + \delta \phi$, where $\delta \phi$ is the potential difference between the particle and the surface. The
probability of electron collection then becomes

\[ P_e = P_i e^{\delta \phi / T_e}, \quad (2) \]

which decreases when \( \delta \phi < 0 \) because electrons are repelled, and increases when \( \delta \phi > 0 \) because electrons are attracted. This mechanism effectively limits the particle's charge fluctuations to a finite range about an average value \( \delta \phi_{\text{ave}} = 0 \).

Potential fluctuations can be related to charge fluctuations \( \delta Q \) by \( \delta \phi = \delta Q / C \), where \( C \) is the capacitance of the particle-surface system. The probability of electron collection is then

\[ P_e = P_i e^{\delta Q / (C T_e)}. \quad (3) \]

The charge on each particle performs a bounded random walk where the probability of gaining an ion (a step to the “right”) is constant, and the probability of gaining an electron (a step to the “left”) is given by Eq. (3). The charging model [Eq. (5)] represents a Markov process [10] for transition probabilities from a charge state \( \delta Q_j = j e, \ j \in (-\infty, \infty) \). Since the Markov process is regular and effectively finite the steady-state distribution of \( \delta Q \) is a normal (i.e., Gaussian) distribution. This is our first result.

Our second result is that the steady state, root-mean-squared value of the charge fluctuation (i.e., the standard deviation of the \( \delta Q \) distribution) is

\[ \frac{\delta Q_{\text{rms}}}{e} = \sqrt{\frac{C T_e}{e}}, \quad (4) \]

which gives the fluctuations in units of \( e \). Consequently, \( \delta Q_{\text{rms}} \) depends only on \( C T_e \). Note that \( \delta Q_{\text{rms}} \) is not given by Poisson statistics for the net number of elementary charges on the dust particle [9], since in our model \( \delta Q_{\text{ave}} \ll \delta Q_{\text{rms}} \). We also find that the steady-state value of \( \delta Q_{\text{rms}} \) is independent of the plasma density, as is the case for isolated particles in plasma [11]. To further characterize the charge fluctuations, we must consider \( C \).

The capacitance of an isolated spherical particle with radius \( a \) is \( C_0 = 4\pi \varepsilon_0 a \), which is valid in plasma when \( a \) is small compared to the Debye length. If the particle is placed a height \( h \lesssim 0.1a \) above a flat conducting plate (Fig. 1), the capacitance increases to [12]

\[ \frac{C}{C_0} \approx \gamma + 1 \ln 2 - \frac{1}{2} \ln \frac{h}{a} > 1, \quad (5) \]

where \( \gamma = 0.5772\ldots \) is the Euler-Mashereone constant. Here \( C \) diverges logarithmically as \( h/a \to 0 \), so that \( C > C_0 \), increasing the range of the charge fluctuations [Eq. (4)].
The capacitance is insensitive to the shape of compact particles when $a$ is taken to be the characteristic particle size \( \overline{a} \). For values typical of Flanagan's experiment [4], $a = 500$ nm, $h = 0.3$ nm, and $T_e = 60$ eV (the primary electron energy), we find $C/C_0 = 4.63$ and $\delta Q_{rms} = 311e$, which greatly exceeds the shared charge.

To determine the temporal behavior of $\delta Q$, the model was solved using a Monte Carlo simulation for an ensemble of $n$ identical particles. For each particle, we start with the initial condition $\delta Q = 0$. For each time step $\Delta t$, we compute two random numbers distributed uniformly in $[0, 1)$. If the first random number is less than $P_i$, then $\delta Q$ is increased by one, representing ion collection. If the second random number is less than $P_e$, then $\delta Q$ is decreased by one, represented electron collection.

For a given value of $CT_e$, we simulated this system for $n = 10,000$ particles vs dimensionless time $t_{\nu_i}$. During the course of the simulation the average charge $\delta Q_{ave}$, the standard deviation $\delta Q_{rms}$, the largest positive charge $\delta Q_{max}$, and largest negative charge $\delta Q_{min}$ were computed for the ensemble. A time history of one simulation run is shown in Fig. 2 for \( CT_e = 5.56 \times 10^{-18} F eV \), which corresponds to the capacitance of an isolated sphere with $a = 20$ nm for $T_e = 1$ eV. Here the average of the charge fluctuations is approximately zero, while the extreme values make excursions of up to $\pm 25e$ away from zero. When a particle’s charge makes a large negative excursion, the electrostatic force may exceed the adhesive force leading to particle release.

The dependence of the dimensionless charging time $t_{\nu_i}$ on $CT_e$ computed using Monte Carlo simulations is shown in Fig. 3. Here $t_r$ is the characteristic time required for an initially uncharged ensemble to approach steady-state. The charging time was found by fitting $\delta Q_{rms}(t)$ with a function $\propto (1 - e^{-t/t_r})$. Our third result is that the charging time increases linearly with $CT_e$ and is well described by the line

$$t_{\nu_i} = (2.05 \times 10^{18} F^{-1} eV^{-1}) CT_e. \quad (6)$$

The charging time in seconds is

$$t_r = (72.6 \times 10^6 m^{-1} eV^{-1}) \frac{C}{a_n c_s T_e} \propto \frac{1}{a_n}. \quad (7)$$

where $a$ is in m, $n_0$ is in $m^{-3}$ and $c_s$ is in m/s. Here $t_r$ is inversely proportional to the particle radius and the plasma density. The inverse dependence on plasma density is consistent with the measured [4] dependence of the particle release time constant. Smaller particles have a longer charging time since they have smaller collecting areas.
Figure 2: Time dependence of charge for an ensemble of $n = 10000$ particles with $CT_e = 5.56 \times 10^{-18}$ F eV. The dashed line gives the asymptotic dependence of Eq. (4).

Figure 3: Dimensionless charging time $t_r \nu_i$ vs particle-surface capacitance $C$ times the electron temperature $T_e$ in eV, determined from Monte Carlo simulations. The data are well fitted by a straight line.
Finally, we can roughly estimate the electrostatic force for a dust particle on an electrically floating surface in a discharge with a bulk component and a low-density energetic electron component \[\text{[1, 4]}\]. For an electrically floating (or dielectric) substrate, the electric field at the surface scales as \(E_w \sim \frac{T_{e,\text{hot}}}{\lambda_D}\), where \(T_{e,\text{hot}}\) is the effective temperature of the energetic electrons and determines the floating potential. For a low-pressure filament discharge, \(T_{e,\text{hot}}\) is roughly the primary electron energy. The Debye shielding length \(\lambda_D \sim \frac{T_{e,\text{hot}}^{1/2}}{n_0^{1/2}}\) is dominated by the bulk electron space charge. Consequently, we predict the electrostatic cleaning force scales as

\[
F \propto \delta Q_{\text{rms}} E_w \sim a^{1/2} n_0^{1/2} T_{e,\text{hot}}^{3/2} T_{e,\text{bulk}}^{-1/2},
\]

which gives a weak scaling with density and radius and a stronger scaling with the tail electron energy. This scaling is supported by the experimental observations \[\text{[1, 4]}\] that particle removal occurs even at low plasma density when there is an energetic electron component. Since the adhesive van der Waals force \(\propto a\), it goes to zero faster than the electrostatic removal force [Eq. 8]. Consequently, there should be no lower limit on the size of particles that can be removed using plasma assisted cleaning.

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