Low energy ion implantation using non-equilibrium glow discharge

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Abstract  The cathode sheath in the pulsed glow discharge plays a key role in defining the energy of ions reaching the wafer. Understanding the structure, dynamics and collisional properties of the sheath is critical for successful application of these discharges to low energy plasma implantation. Measurements of the time resolved ion energy distribution in the cathode sheath of the dc pulsed discharge through boron trifluoride were performed both for collisional and collision-less sheath. In the case of a collision-less sheath, ion energy distribution is dominated by the high energy peak. For the collisional sheath, ion energy distribution is influenced by the complexity of elastic and inelastic collisions. The measured BF$_2^+$ ion energy distributions for different number of collisions in the sheath are consistent with a charge transfer model. Computations using Davis and Vanderslice model confirmed that charge transfer is a major inelastic collision process in the sheath. However, the experiments indicate that other inelastic ion-atom collisions resulting in BF$_2^+$ dissociation inside the sheath cause a breakdown of the charge transfer model. Experimental ion energy distributions were also used to compute the dopant profile distribution in the silicon. A remarkable agreement between the calculated and experimental depth profiles is achieved.

1. Introduction:
In the past three decades, the speed and packing density of integrated circuits have dramatically increased following Moore’s law, which predicts that the number of transistors is multiplied by four every three years. The semiconductor device dimensions continue to shrink in order to meet the power and price requirements. This brings many technological challenges and constraints for each new device node. For example, in order to reach the new doping requirements for the source drain extension, the ion implantation energy needs to be further reduced with a higher dopant concentration. The physical limitations (space charge during beam transport) of the traditional beamline approach are reached, and new beamline techniques such as ion implantation with a deceleration mode, are being developed. Unfortunately, this method suffers from energy contamination for very low-energy implantation, causing deeper junction depth than expected. Plasma-based ion implantation is emerging as a viable technique that can meet the doping requirements of future devices if associated with an adequate dopant activation technique [1].

The first plasma implantation apparatus built by Strack [2], used a silicon wafer immersed in diborane or phosphine glow discharge diluted in 99% hydrogen. The wafer was installed on the cathode and surrounded by a silicon or graphite cylinder to enhance the plasma density. In this system
the wafer could be simultaneously heated during the implant. The dose and the dopant diffusion into the wafer were controlled by the implant time. The implant voltage was in the range of 700 to 1200 V, so that the dopant was deposited primarily in a shallow surface region. This technique led to higher diffusion rates than the classical diffusion technique, but the lack of independent dose and depth control, as well as the poor beam species purity, made this approach less attractive than beamline implantation.

Later on, Conrad et al. [3] developed Plasma Immersion Ion Implantation (PIII) system that uses an ionized gas surrounding an irregular surface at high negative voltage. In PIII system, the workpiece is directly immersed inside the glow discharge, which is created through a negative pulse voltage. A plasma sheath forms around the workpiece. Ions are then implanted conformally into the workpiece as long as the sheath dimensions remain less than the workpiece feature sizes. The motion of the propagated sheath is described quasi-statically by the Child Langmuir law. This theoretical work has been done by Conrad and Lieberman [4, 5] for PIII in planar geometry, and modified by Scheuer et al [6] in planar, cylindrical and spherical geometry. It led to improved knowledge of the implanted ion current, ion energy, surface electric field and secondary electron coefficient in the control of the process. Nowadays, PIII is used in the semiconductor research industry, for conformal doping of trench sidewalls [7, 8, 9] and junction fabrication [10]. New applications include material modifications or semiconductor doping. More details on the history of PIII can be found in [11, 12, 13].

Another alternative for low energy ion implantation is to use a Pulsed Plasma Doping (P2LAD) system that was developed by Varian Semiconductor Equipment Associates (VSEA). This system offers the capability of operating at very low energies (0.1 < ε < 10 keV) and accurately measures the implanted dose using an annular Faraday cup located near the wafer. Through this technique, the silicon wafer is directly immersed in the pulsed d.c. glow discharge. Each negative cathode pulse establishes the discharge by creating an electric field in the sheath region that accelerates ions into the wafer. The energy of the ions is defined by the cathode fall voltage applied onto the wafer. The pulsed nature of the discharge, duty cycle and pulse width control the plasma exposure of the silicon wafer thus minimizing the etching of the substrate [14]. The secondary electrons emitted from the cathode during the pulse on period are accelerated by the cathode high voltage and can gain enough energy to ionize neutral gas particles during their travel through the sheath. When the pulse ends the discharge follows a natural decay process. Boron or boron molecular ions (BF$_x^+$, B$_x$H$_y^+$) are the most common dopants used for p-type doping, while arsenic or arsenic molecular ions, or phosphorus ions are more commonly used N-type dopants.

An example of the VSEA plasma-based ion implantation machine, PLAsma Doping (PLAD) system, is shown in Fig. 1 [15].

![Figure 1. PLAD System](image)
In this paper we discuss the basics and principles of the plasma ion implantation technique. We also discuss the diagnostics and characterization of the plasma-doping system in a BF$_3$ discharge. A different collision processes occurring inside the high-voltage sheath and a description of the energy distribution of ions reaching the cathode is presented here.

Finally, a model based on ion energy distribution measurements, allowing for the prediction of the dopant depth profile is presented and validated by comparison to Secondary Ion Mass Spectrometry (SIMS) measurements.

2. Basics and principles of the plasma ion implantation technique

2.1. Description of a high voltage sheath

When a negative high voltage pulse is applied to the target, electrons near the surface are initially driven away from the cathode during the time scale of the inverse electron plasma frequency $\omega_{pe}^{-1}$, leaving behind a uniform ion density known as the ion “matrix” sheath [5]. On the time scale of the inverse ion plasma frequency $\omega_{pi}^{-1}$, ions present inside the sheath are accelerated toward the target. This, in turn, drives the sheath-plasma edge farther away, exposing to the electric field new ions that are extracted. On a longer time scale, the system evolves toward a steady state Child law [16] sheath. The electron and ion plasma frequencies are defined by the following equations:

$$\omega_{pe} = \left(\frac{e^2 n_e}{\varepsilon_0 m_e}\right)^{1/2}, \quad \omega_{pi} = \left(\frac{e^2 n_i}{\varepsilon_0 M_i}\right)^{1/2}$$

where $n_e$ is the electron density, $m_e$ is the electron mass, $\varepsilon_0$ is the permittivity of free space, $n_i$ is the ion density and $M_i$ is the ion mass.

In the case of PIII, the plasma steady state is created by an RF source of constant plasma density, and each negative pulse applied on the wafer accelerates the ions from the bulk plasma up to the wafer target. In the PLAD case the plasma is ignited periodically by the negative pulse applied to the cathode, therefore the plasma density does not remain constant during the whole period. The Lieberman’s model is slightly modified here, so as to take into account the evolution of the plasma density during the pulse. In both cases, when a negative voltage is applied unto the cathode, on a very short time scale, a matrix sheath is formed. The voltage drop inside the sheath is large compared to the bulk plasma electron temperature. As the potential in the sheath is highly negative with respect to the plasma, it is assumed that only ions are present inside the sheath of thickness ($s$) with a uniform ion density ($n_i = n_s$). The matrix sheath thickness can be estimated using the following formula [17]:

$$s = \left(\frac{2\varepsilon_0 V_c}{en_s}\right)^{1/2}$$

where $n_s$ is the ion density inside the sheath. Lieberman estimated that the time ($t$) required to implant all the ions of the matrix sheath was proportional to the inverse of the ion plasma frequency [5]:

$$t \approx \frac{2.7}{\omega_{pi}}$$

The electron and ion plasma frequencies as well as the time necessary to implant all the ions from the matrix sheath for different plasma density is presented in Table 1.
As mentioned previously, in the case of the plasma doping system, the ion density is not constant during the entire pulse period. Typical ion density before the beginning of the negative pulse is between $2 \times 10^8$ and $5 \times 10^8$ ions/cm$^3$. All the ions of the matrix sheath are implanted in less than 1 s, therefore matrix sheath is not considered important in the plasma doping case.

Immediately following the matrix sheath, ions are accelerated toward the cathode. This drives the sheath-plasma edge further away. In case of collision-less motion of ions inside the sheath, calculation of the time taken to reach the stable Child law sheath can be performed. Consequently, the potential inside the sheath follows a $x^{4/3}$ dependence [18]:

$$\phi(x) = -\frac{3}{2} \left( \frac{j_c}{\epsilon_0} \right) \frac{M}{2e} \times \left( \frac{v_0}{s} \right)^{4/3} \times x^{4/3}$$

{1.5}

where $j_c$ is the current density, $\epsilon_0$ is the free-space permittivity, $e$ and $M$ are the ion charge and mass and $x = 0$ at sheath edge.

The Child law current density $j_c$ for a voltage $V_c$ across a sheath thickness ($s$) is defined by the following equation [16]:

$$j_c = \frac{4}{9} \frac{e_0}{M} \times \left( \frac{2e}{M} \right)^{1/2} \times \frac{V_c^{3/2}}{s^2}$$

{1.6}

Assuming that there are two sources of ions in the sheath (ions streaming into the sheath at the Bohm velocity and ions uncovered by the expanding sheath) and equating $j_c$ to the charge per unit time crossing the sheath boundary we obtain [4]:

$$e n_0 \left( \frac{ds}{dt} + u_B \right) = j_c$$

{1.7}

For a constant plasma density, the motion of the pulsed plasma sheath ($s$) in a collision-less PIII follows this equation:

$$e n_0 \left( \frac{ds}{dt} + u_B \right) = \frac{4}{9} \frac{e_0}{M} \times \frac{2e}{M} \times \frac{V^{3/2}}{s^2}$$

{1.8}

where $e$ is the ion charge, $n_0$ is the plasma density in the bulk, $s$ is the sheath thickness, $u_B$ is the Bohm speed, $\epsilon_0$ is the permittivity of free space, $M$ is the ion mass and $V$ is the applied voltage.

In PLAD case, the bulk plasma density is not constant during the entire pulse, the equation which takes into account the plasma density variations $n(t)$ is as follows [19]:

$$e n(t) \left( \frac{ds}{dt} + u_B \right) = \frac{4}{9} \frac{e_0}{M} \times \frac{2e}{M} \times \frac{V^{3/2}}{s^2}$$

{1.9}

The time scale ($t_c$) for establishing the steady-state Child law sheath is then [17]:

Table 1: Electron and ion plasma frequency, matrix sheath time length after the beginning of the pulse as a function of the plasma density [15]
The time necessary to establish the steady-state Child law sheath for different plasma density and cathode voltage is calculated in Table 2. As can be seen, the time needed to reach the steady-state sheath is dependent on the plasma density and cathode voltage. The steady state is reached faster at higher plasma densities and lower cathode voltages. In most of the cases studied here, a quasi steady state sheath is reached during the first 10 µs of the high-voltage sheath.

Table 2: Time necessary to establish the steady-state Child law sheath for different plasma density and cathode voltage

| Cathode Voltage (V) | Plasma density (cm⁻³) |
|---------------------|-----------------------|
|                     | 2.0E+08   | 5.0E+08   | 1.0E+09   | 2.0E+09   | 5.0E+09   |
| 250                 | 6.2        | 4.0        | 2.8        | 2.0        | 1.2        |
| 500                 | 10.5       | 6.6        | 4.7        | 3.3        | 2.1        |
| 1000                | 17.7       | 11.2       | 7.9        | 5.6        | 3.5        |

An example of a calculated sheath thickness as a function of time is presented in Fig.2 for a 1 kV 40 mTorr BF₃ glow discharge.

Figure 2: Sheath thickness calculated using (1.9) for a 1 kV 40 mTorr BF₃ glow discharge the plasma parameters, such as n(t), were measured by a Langmuir probe [15]

The cathode voltage and temporal evolution of the plasma parameters measured by the Langmuir probe were used as an input for the calculation, assuming a collision-less sheath. With an increasing dc bias voltage, the sheath expands. As the dc bias voltage and the bulk plasma density reach a steady state, the sheath thickness tends to a constant value.

In the more realistic case of BF₃ discharge one needs to consider collisions in the sheath. Consequently, when the ion motion is collisional, the Child law can be written as follows [18, 20, 21]:

\[
    j_i = e_0 \left( \frac{2}{3} \right) \left( \frac{e}{M} \right)^{3/2} \frac{2e\lambda_i}{\pi M} \left( \frac{2e\lambda_i}{\pi M} \right)^{1/2} \frac{V_0^{3/2}}{s^{3/2}}
\]  

where \( e_0 \) is the permittivity of free space, \( e \) is the charge of an ion of mass \( M \), \( V_0 \) is the cathode voltage, \( \lambda_i \) is the ion mean free path and \( j_i \) is the ion current density. The sheath potential \( \phi(x) \) at a distance \( x \) inside the sheath can be expressed by the following equation (\( x = 0 \) at sheath edge):
The number of collisions \( s/\lambda \) inside a sheath is calculated using the following formula:

\[
\frac{s}{\lambda} = \frac{1}{3} \times \left( \frac{e}{\pi M} \right)^{2/5} \times \left( \frac{e_0}{j_i} \right)^{2/5} \times (10V)^{2/5} \times \left( \frac{\sigma \times p}{kT_g} \right)^{2/5}
\]

where \( \sigma \) is the ion neutral cross-section, \( k \) is Boltzmann’s constant, \( T_g \) is the gas temperature and \( p \) is the neutral gas pressure.

Ion processes inside a collisional and collision-less sheath are depicted in Fig. 3.

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Figure 3: Representation of the different particle interaction in a collision-less sheath or collisional sheath [15]

In the same figure the secondary electron emission process and the interactions of secondary electrons with the gas phase is shown. A relative importance of different collisions in the sheath can be understood only after considering elastic polarization scattering, charge transfer, molecular ion dissociation and ionization occurring inside a collisional sheath.

### 2.2. Principle of the operation

As previously stated the glow-discharge PLAD chamber consists of a cathode, which holds the wafer being implanted, and an anode (see Fig. 4). A negative DC voltage pulse is applied to the cathode, which generates a glow discharge in the volume adjacent to the wafer.
The discharge is ignited by each voltage pulse applied to the wafer. When the pulse ends, the discharge follows a natural decay process. During the pulse-on period, ions in the plasma are accelerated by the electric field across the sheath and are subsequently implanted into the wafer. The energy of the ions striking the wafer during the pulse-on period is mainly controlled by the applied voltage. Other parameters, such as pulse width, frequency, gas pressure, flow rate, surface condition and the geometry of the electrodes, can also affect the implant process by changing the plasma composition, the ion flux and the number of collisions inside the sheath. Short pulse-on periods provide short plasma exposure, no accumulation of charges and control of etching and deposition effects while maintaining high dose rates at low energies (<1 keV) [14].

In the DC plane parallel electrode system such as PLAD, the breakdown voltage is a function of the product of pressure and electrode distance (P×d). In Fig. 5 the experimental Paschen curves for BF₃ are shown. For small (P×d) the limiting value of (P×d) occurs at voltages greater than 1 kV. The curves at different cathode to anode distances all have similar behavior driven by the secondary electron emission. When the anode-to-cathode distance is small or the pressure is low, the secondary electrons emitted from the cathode can reach the anode while undergoing only a small number of collisions and do not create a sufficient number of ions for the regeneration of secondary electrons. When the pressure is high, the electrons cannot acquire enough energy between collisions to produce enough ions.

If the distance between the electrodes is greater than 10 cm, only a small fraction of the produced ions will be able to reach the cathode with sufficient energy to create more secondary electrons. At both extremes of the P×d product value, the probability of ionization is small and the breakdown voltage required to ignite the discharge is high. The breakdown voltage reaches a minimum between the two extremes around 450 V. At lower current densities BF₃, discharge adjusts itself to the stable value of (d), while in the case of high current density the abnormal glow regime dominates.

The pulsed glow discharge cannot be operated below 450 V unless an external plasma source is used. A hollow cathode ring (HC), as shown in Fig. 4, is used as an external plasma source to self-sustain the discharge for low-energy implantation. The HC assembly is composed of a 10 cm tall aluminum spray coated silicon ring installed between the anode and cathode. The ring which has a radius of 25 cm is positioned at 2.5 cm from the cathode. The moveable anode can penetrate inside the HC ring. The HC is negatively pulsed with a dc power supply that can be synchronized to the cathode voltage pulse. The large surface area of the cathode for a given discharge current plays a significant role here. The cathode sheath is confined to a narrow layer between the cathode ring and the slightly smaller electrode cathode. In this configuration the basic trapping mechanism of secondary electrons between sheaths is well preserved. In addition, the hollow cathode ring provides a mirror electric field for electrons thus enabling the electron-confinement mechanism. It is also used to increase the plasma...
density. The HC discharge can be operated at low pressure, even at very low cathode voltages (up to 50 eV) with high ion current density (see Fig 6). The advantage of operating at low pressures is to increase the ion-neutral mean free path and to reduce the number of collisions inside the sheath.

Figure 5: Experimental Paschen curves showing the evolution of the breakdown voltage of a BF$_3$ discharge as a function of the product $P \times d$ [15]

Figure 6: Ion current density as a function of cathode bias voltage and anode-to-cathode spacing at 30 mTorr for a hollow cathode plasma operated at -1500 V [15]
Figure 7: Electric field distribution calculated using Opera 3D with -500 V on the cathode and -1500 V on the hollow cathode for two different anode-to-cathode spacings (100 and 35 mm) [15]

In order to investigate the effect of cathode-to-anode spacing on the electric field distribution we have used Opera 3D electromagnetic code [26]. We have calculated the field distribution in the hollow cathode (Fig. 7) and powered anode case (Fig. 8). When the anode-to-cathode spacing is reduced (See Fig. 7), the effective hollow cathode surface area is decreased. Reducing the effective hollow cathode surface implies a reduction of the cathode current and the plasma density decrease. Larger anode-to-cathode spacing produced higher plasma density which leads to higher current as indicated in Fig. 6. The anode-to cathode gap is used here to control the plasma density and uniformity. In most cases, the HC voltage is set as around -1500 V and is coincident with the cathode pulse, so that no time delay is introduced between the pulses. This configuration has been found to maximize the plasma density and uniformity.

In another configuration negative voltage is applied to the anode while the walls and the hollow cathode (HC) are at the ground potential. The anode is pulsed synchronously with the cathode pulse up to -1500 V. As can be seen on Fig. 8 the electric field is uniform near the cathode.

Figure 8: Electric field distribution calculated using Opera 3D with -500 V on the cathode and -1200 V on the anode for an 5cm anode-to cathode spacing [15]

The external electric field distribution as shown on Figs. 7-8 is distorted by space charge distribution in the discharge. Correspondingly three different regions form between the anode and the cathode: the anode region, the bulk and the cathode region. Inside the bulk, the flow of positive and negative carriers is balanced by a plasma potential ($V_p$). In the case of BF$_3$, negative plasma potential was obtained for various plasma parameters [19]. This was attributed to the dominant role of negative charge carriers being an ion as opposed to electrons. The results indicate that the negative ion densities
are the same order of magnitude or higher than electron density. The main mechanism of removing electrons is via attachment that is not accompanied by detachment. Diffusional losses are small and recombination is dominated by attachment, in particular in the early phase of the pulse on period.

As expected only electrons having sufficiently high energy can penetrate through the sheath and reach the surface. Since the sheath is at a negative potential relative to the bulk plasma, it tends to repel the electrons and negative ions. The positive ions are accelerated across the sheath and implanted into the target with an energy lower than or equal to \( V_0 + V_p \times e \).

The high-voltage pulse applied to the cathode is generated by a high-voltage dc power supply. Fig. 9 shows an example of voltage waveforms measured during a 1 kV, 2.5 kHz, 40 mTorr BF\(_3\) discharge [22].

![Figure 9: Cathode voltage and current waveforms for a 1kV, 40mTorr, 50 s, 2.5 kHz BF\(_3\) discharge](image)

The typical high voltage rise and fall times are 1 to 5 \(\mu\)s and 5-30 \(\mu\)s, respectively, at operating pressures of 10 – 300 mTorr, with a pulse width of 10 to 50 \(\mu\)s and a 1 to 15 % duty cycle.

In this case, the measured cathode current \(I_c\) is a combination of ion current \(I_{ions}\), electron current \(I_e\), secondary electron current \(I_{sec}\) and the displacement current \(I_{disp}\).

\[
I_c = I_{ions} + I_e + I_{sec} + I_{disp} \quad {1.14}
\]

Since the electron density is small compared to the ion density inside the sheath, the electron current measured on the cathode is negligible.

\[
I_e = I_{ions} + I_{sec} + I_{disp} \quad {1.15}
\]

At the end of the pulse, the available electrons neutralize the wafer surface charge, which has built up during the voltage pulse. The pulse width is limited by the need to maintain the charge-up voltage below the damage threshold [23, 24].

The secondary electron current is related to the electron emission after the energetic ion impact on the cathode and can be expressed as follows:

\[
I_{sec} = \gamma \times I_{ions} \quad {1.16}
\]

The number of electrons ejected per incident particle i.e. the secondary electron coefficient was determined experimentally as a function of the cathode voltage (i.e. ion energy). As can be seen in Fig. 10, when the voltage is raised the number of electrons ejected by the incident ions is increased.
It is also noticeable that the fast neutrals created through charge exchange collisions inside the sheath may contribute to secondary electron production. However, for low energies (< 1keV), experimental results suggest that electron emission induced by the neutral bombardment is negligible compared to the electron emission induced by the ion bombardment [25].

3. Diagnostics for PLAD plasma characterization

A mass spectrometer was used to measure in-situ the Ion Energy Distribution (IED) of the different ions reaching the cathode during plasma-based ion implantation. The Electrostatic Quadrupole Probe (EQP) analyzer from Hiden Analytical Inc. was installed inside the high voltage cathode as shown in Fig 11 [15]. Here, the cathode can be negatively pulsed between 0.1 kV to 5 kV and the mass spectrometer can float between 0 and -1 kV.

A 200 mm silicon wafer with an aperture in its center was introduced under vacuum inside the process chamber. When the discharge is on, the ions are extracted directly from the plasma through the aperture. The extractor aperture was set to 2 mm (Fig. 12) to achieve a good transmission and a good pumping speed. By using a differential pumping system, a base pressure of 2x10⁻⁸ Torr inside the mass spectrometer can be achieved.
Hiden EQP mass spectrometer system consists of an electrostatic ion energy analyzer followed by a quadrupole mass spectrometer. A three-dimensional (3D) electrostatic model of the mass spectrometer has been developed to optimize the transmission efficiency of the ions and minimize the effects of field perturbations and gas collisions. Fig. 12 shows a picture of the model developed here. It is composed of the extraction optics, the drift tube, the quad lens, the energy analyzer and the focusing lens [26]. In the past, electrostatic simulations [21, 27, 28] were made using two-dimensional electrostatic models reaching up to the entrance of the energy analyzer. However, the non-linear parts of the mass spectrometer, such as the quadrupole lens in front of the energy analyzer, need to be simulated using a three dimensional (3D) models. The 3D electrostatic fields and particle trajectories with space charge are necessary for designing high precision spectrometers.

In this experiment, the flat extraction lenses normally used were replaced by a conical Pierce-angled optics and the inter-electrode gaps between the extractor and the cathode were modified. The new geometry, in addition to lowering perturbations of electric field, also allows for better gas pumping thus lowering losses due to collisions. Based on the mass spectrometer simulations, the extraction sector electric potential distribution was modified [15]. The modified spectrometer operates in a more efficient way that is suitable for the in-situ diagnostics of pulsed DC plasma and allowed real time collection of the ion species from the cathode sheath during the pulse-on period.

Under the experimental conditions used here (V\textsubscript{cathode} = -1000 V to 0 V), all ions with a normal incidence angle had 100 % transmission efficiency inside the mass spectrometer up to the entrance of the quadrupole. The results of simulation of the transmission efficiency of BF\textsubscript{2}\textsuperscript{+} ions when using various entrance angles ranging from 0.5 ° to 5.5 ° is shown in Fig.13. The experimental calibration of the EQP during a 500 V 100 mT PLAD implant was used as an input for the simulation. The transmission efficiency was 100% for incident angles up to 1 °, while it decreased rapidly for incident angles greater than 2 °. However, under our experimental conditions, ions are calculated to have a low incidence angle (< 1 °) [29].
Due to the pulsed nature of the plasma, its characteristics change over time during its rise time and decay. Therefore, time-resolved measurements are necessary. In order to perform a time resolved acquisition, the mass spectrometer and the Langmuir probe were synchronized with the discharge pulse [30]. A time resolution of up to 5 μs was achievable with the mass spectrometer and 1 s with the Langmuir probe. The Langmuir probe was located at 4 cm away from the silicon wafer and was used to measure radially the plasma parameters from the center of the wafer up to the process chamber wall.

Fig. 14 shows an example of the time development of the probe characteristic measurements in a BF3 plasma during a 1 kV, 40 mT, 30 μs pulse width at a frequency of 2500 Hz. In principle, the electron saturation current increases during the pulse-on period and then slowly decreases during the afterglow period, showing the increase and decrease of plasma density at ignition and extinguishing of the DC plasma. The details of the radial distributions of plasma parameters using the Langmuir probe will be discussed on the next section.

Figure 13: BF2⁺ transmission efficiency inside the mass spectrometer modeled with different cone angle at the entrance of the EQP with the experimental settings of a 500V 100mT PLAD implant [15]

Figure 14: Pulse-on period (a) and afterglow (b) time resolved Langmuir probe for a 1kV 40mT 30 s BF3 implant,
4. Plasma Composition and Ions Reaching the Cathode

The results of the temporal development of the radial electron density distribution was obtained under the same BF$_3$ glow discharge using the Langmuir probe measurement at different radial positions inside the process chamber (see Fig 15).

![Figure 15: Time evolution during the pulse-on period of the electron density radial distribution measured by the Langmuir probe during a 1 kV 40 mTorr 30µs BF3 glow discharge [15]](image)

At the beginning of the pulse, the electron density is uniform. The electron density increases with time during the pulse-on period. As can be seen, during the whole pulse, the electron density is uniform in the area near the wafer and strongly decreases at the edge of the cathode (radial distance equal to 200 mm). A small drop in the electron density is observed at about 120 mm from the centre of the wafer, which is where the annular Faraday cup is positioned. As discussed previously, the Faraday cup is used to measure charge deposited unto the wafer. The cup is magnetically suppressed so that secondary electrons emitted by the ions stay inside the cup. These electrons cannot participate in the ionization, and the electron density is only locally reduced.

As can be seen, the plasma potential is quickly stabilized after the beginning of the pulse. The plasma potential fluctuations measured above the wafer plane were not more than 1 eV. However, the plasma potential drops at the edge of the cathode.

The temporal development of the radial ion density was also extracted from the I-V curve measured at different radial positions inside the process chamber, and is depicted in Fig 16.
As discussed previously, the ion density stabilizes after 15 µs from the beginning of the pulse and does not change up to the end of the pulse. In essence, these time evolution measurements confirm stable conditions throughout the implant. In contrast, the low energy population of electrons increases and reaches a steady state only after 40 µs. This observation may be explained by the presence of negative ions at the beginning of the pulse. The ion density is uniform across the wafer but some uniformity distortions can be observed at the edge of the wafer. Higher $n_i$ can be detected above an interface ring located between the edge of the wafer and the Faraday cup. This interface contributes to the secondary electron emission thus compensating for the $n_i$ decrease at the edge of the cylindrically symmetric discharge.

An accurate IED measurement during the rise time and fall time of the cathode pulse is not possible because of the time-step resolution limitation of the mass spectrometer. However, during these dynamic changes, the number of ions detected by the mass spectrometer is still accurate (only the exact energy of each ion is unknown) and the relative ion flux measured remains valid.

The time evolution of the ion fluxes of different ions measured by the mass spectrometer during the discharge pulse is shown in Fig. 17 (Ion flux is defined here as the integral of the measured IED). During the first 10 µs of the pulse-on, the sheath is expanding and the relative ion flux is increasing. After 15 µs, the relative total ion flux is stabilized and the IED of the different ions remain the same. During the decay, the total ion flux decreases as the sheath collapses. $BF_2^+$ is the most abundant ion implanted into the wafer and represents more than 60% of the total ion flux. The $B^+$, $BF^+$, and $BF_2^+$ ions make more than 98% of the total flux, while $BF_3^+$ is less than 2% of the total ion flux.
The B+, BF+, BF2+ and BF3+ ion energy distributions for a 500 V, 30 mTorr, BF3 discharge at five different anode-to-cathode spacings are depicted in Fig. 18. The general shape of the ion energy distribution for spacing lower than 40 mm, is consistent with a collisional sheath. On the other hand at spacing greater than 40 mm the ion energy distribution of the B+, BF2+ and BF3+ is peaked at energy defined by the cathode bias voltage.

The BF3+ ion energy distribution is collisional and consistent with many collisions that this ion experiences in the sheath.

An example of measured ion energy distributions in BF3 pulsed discharge of the ions that cross the high-voltage sheath is shown in Fig. 19. The relative flux of positive ions was measured in a highly collisional sheath. From the shape of IEDs, one can infer that positive ions undergo several elastic collisions in the sheath and have low energies, with ion-neutral charge exchange being a dominant collision. The symmetric and asymmetric charge exchange collisions dominate in the sheath thus producing several ion species as shown in Fig. 19.

Only B+ ion energy distribution is an exception to this rule. In this case the dissociation of heavier ions into lighter ion has to be taken into account. The tail of the B+ distribution can be understood as velocity and momentum is higher for this ion than any other ion in the sheath.

In order to explain the shape of the BF+, BF2+ and BF3+ IEDs a modified Davis and Vanderslice model was used here. Davis and Vanderslice accurately measured and modeled the ion energy distribution for a cathode sheath during a dc glow discharge in noble gases [31]. Their model illustrated in Fig. 19 assumes that no ionization occurs inside the sheath, that charge exchange is the only ion-neutral collision mechanism and momentum transfer is negligible.

As previously mentioned the sheath potential is governed by the Child’s law [5]. Consequently the equation that describes the ion flux distribution is given by:

\[ \Phi(x) = (V_c - V_p) \times \left( 1 - \frac{x}{s} \right)^{\frac{3}{2}} + V_p \]  

\[ \{3.1\} \]
Figure 18: $B^+$, $BF^+$, $BF_2^+$ and $BF_3^+$ IED normalized to the total ion flux for anode-to-cathode spacing for a 500 V, 30 mTorr, 5 sccm, 2500 Hz $BF_3$ glow discharge created using the hollow cathode at 1400 V.

Figure 19: $B^+$, $BF^+$, $BF_2^+$, $BF_3^+$ IED normalized to the total ion flux for a 500 V $BF_3$ plasma at 100 mTorr and 2500 Hz.

In their original paper, Davis and Vanderslice assume there is a linear electric field. According to equation (3.1) the potential in the sheath should have a $x^{2/3}$ dependence.
As shown in Fig 20, an ion that strikes the cathode, with an energy $eV_x$, has to undergo a charge transfer collision at a point $x$ and then travel all the way to the cathode without further collision. Making the mean free path for a charge exchange as $\lambda_i$ and assuming that $\Phi_0$, the ion flux at the sheath edge, remains constant all the way to the cathode, the number of collisions per surface and time units that occur in the region $dx$ is $\phi_i(dx/\lambda_i)$. The probability for any of these ions to reach the cathode without further charge exchange is given by $e^{-x/\lambda_i}$. The number of ions per surface and time units detected at energy $eV_x$ is then given by:

$$d\phi = \left(\frac{\phi_0}{\lambda_i}\right) e^{-x/\lambda_i} dx$$

Using equation {3.2} and setting $\Phi(x) = V_x$, the following equation is obtained:

$$x = s \left[ 1 - \left(\frac{V_x - V_p}{V_c - V_p}\right)^{\gamma/\lambda} \right]$$

and

$$dx = -\frac{3s}{5} \left[ \frac{V_x - V_p}{V_c - V_p} \right]^{-\gamma/\lambda} d\left(\frac{V_x - V_p}{V_c - V_p}\right)$$

By substituting {3.3} and {3.4} into {3.2} the modified Davis and Vanderslice equation {3.5} is obtained giving a theoretical expression for IEDs [15]:

$$\frac{1}{\phi_0} \times dV_x = \frac{3s}{5} \times \frac{1}{\lambda_i} \times \left(\frac{V_x - V_p}{V_c - V_p}\right)^{-\gamma/\lambda_i} \times \exp\left[ -\frac{s}{\lambda_i} \left(1 - \left(\frac{V_x - V_p}{V_c - V_p}\right)^{\gamma/\lambda_i}\right)\right]$$

The fraction of ions that cross the entire sheath without any collisions, $e^{-x/\lambda_i}$, is not included in the equation {3.5}. The controlling parameter of the equation is $s/\lambda_i$, which is the mean number of collisions that an ion undergoes on its way through the sheath. An example of calculated ion energy distribution for different numbers of collisions inside the sheath ($s/\lambda_i$ from 1 to 100 collisions) is given in Fig. 21.
Figure 21: Computed ion energy distributions for different numbers of collisions inside the sheath (from 1 to 100). All the curves have been normalized at $E = 0$ eV [15]

It should be noted that the high energy ion fraction decreases rapidly when the number of collisions inside the sheath increases.

From the IED, the mean ion energy can be calculated for different numbers of collisions using the following formula:

$$\langle E \rangle = \frac{\int E \times f(E) \times dE}{\int f(E) \times dE} \quad \{3.6\}$$

As expected, the mean ion energy is reduced when the number of collisions inside the sheath increases (see Fig. 22). It should be noted that only three collisions are enough to decrease $\langle E \rangle$ to $E_{\text{max}}/2$.

Figure 22: Calculated mean energy as a function of the number of collisions based on the Davis and Vanderslice model [15]

The modified Davis and Vanderslice model will be used here to fit the experimental IEDs measured in the BF3 discharge. Only BF2+ will be considered for this calculation as it is the dominant ion under all the various conditions. The hard sphere model is used to estimate the ion-neutral cross section for a BF2+ ion. A constant ion neutral cross-section of $2 \times 10^{-15} \text{cm}^2$ is assumed.

When the glow discharge is operated in the PLAD chamber, a collision-less sheath is not achievable due to the pressure limitation and the low plasma density. Consequently, the discharge is
always operated in a collisional mode. The number of collisions inside the sheath is a relevant parameter that drives the IED shape and describes well the experimental conditions in the case of collisional sheath.

Figure 23: B⁺, BF⁺, BF₂⁺ and BF₃⁺ mean energies normalized to the cathode voltage, as a function of the number of collisions for various BF₃ glow discharge conditions [15]

Fig. 23 shows the ion mean energy as a function of the number of collisions inside the sheath for various BF₃ glow discharge conditions. At lower pressures and higher cathode voltages, higher ion mean energies are achievable. When the sheath is highly collisional (s/λ > 5 collisions), the distribution is peaked at lower energy (Fig. 19). IED during the 500 V cathode voltage pulse for different pressures (from 100 to 250 mTorr) has been fitted with the modified Davis and Vanderslice model by adjusting the number of collisions inside the sheath. The number of collisions obtained with the model is also presented in Fig. 24.

Figure 24: Normalized BF₂⁺ IED in the case of a high-pressure, low-energy (500 V) BF₃ discharge under different operating pressures (100, 150, 200 and 250 mTorr), fitted with the modified Davis and Vanderslice model (DVS) by adjusting the number of collisions inside the sheath

The shape of the measured BF₂⁺ IED is consistent with the calculated one and therefore proving that the symmetric charge exchange between BF₂⁺ and BF₂ is a dominant process in the sheath.

The number of collisions inside the sheath based on the Davis and Vanderslice model is shown in Table 3. As can be seen the number of collisions calculated using the model does not match the one
calculated using the ion current density in a collisional sheath. $s/\lambda$ is higher in the case of the VDS model (see Table 3).

| Pressure (mTorr) | $s_{\text{measured}}$ (cm) | $s/\lambda$ (calculated) | $s/\lambda$ (VDS) |
|-----------------|-----------------------------|--------------------------|--------------------|
| 100             | 1.15                        | 7.4                      | 15                 |
| 150             | 0.9                         | 8.6                      | 18                 |
| 200             | 0.74                        | 9.6                      | 21                 |
| 250             | 0.65                        | 10.4                     | 25                 |

Table 3: 500V high pressure, $s/\lambda$ calculated based on BF$_2^+$ hard sphere model, $s/\lambda$ measured with Davis and Vanderslice (VDS)

As already explained, the fraction of BF$_2^+$ reaching the cathode is significantly lower than the BF$_2^+$ bulk fraction in case of highly collisional sheath. Moreover, the B$^+$ and BF$^+$ fractions are higher at the cathode under the same conditions. This is a strong indication that BF$_2^+$ dissociates inside the sheath and creates B$^+$ ions and possibly BF$^+$ ions [15]. Consequently, charge exchange is not the only inelastic process affecting the shape of the ion energy distribution. This additional mechanism could explain why the Davis and Vanderslice model overestimates the number of collisions inside the sheath.

5. Dopant Profile Simulation

In plasma based ion implantation the resulting dopant profile is dependent on the relative abundances of different ion species extracted from the cathode sheath. In addition, ion energy distribution for each ion species and associated ion-neutral collisions in the sheath have to be known in order to predict a dopant profile.

In this paper we have computed boron dopant profile based on the measured ion energy distribution (IED) of various ions sampled from the sheath of the dc pulsed discharge through BF$_3$. A comparison is being made with experimentally determined secondary ion mass spectrometric (SIMS) profiles. The ion mass and energy distributions were measured in-situ in the center of the wafer using an ion-mass and energy spectrometer. A computer simulation was used to predict dopant profiles for all species and energies allowed by a particular value of the cathode bias voltage.

As soon as the cathode voltage pulse is applied, a dynamic process starts in the discharge chamber, during which the neutrals and charged particles adjust their quantity, position and energy until a steady state is reached. Characterizing this dynamic process is difficult [19]. One concern associated with the pulse rise and fall times is that they may affect the ion mass and energy distribution, thus changing the implant profile. This concern was ruled out in early studies of low-energy BF$_3$ PLAD implantation, as boron SIMS profiles showed no difference for various pulse-on widths (20 to 60 µs) [14] with constant rise and decay times. The IEDs change during the rise and fall times of the pulse-on but the ion density and energy are much lower than during the flat part of the pulse and contribution to the dopant profile is low. In Fig. 17, the time evolution for the different ion fluxes measured with the mass spectrometer during the PLAD pulse are reported. During the first 15 µs of the pulse-on, the sheath expands and the relative ion flux increases. After 15 µs, the relative total ion flux stabilizes and the IEDs of the different ions remain the same. During the decay, the total ion flux decreases as the sheath collapses. Only the constant portion of the pulse will thus be used to calculate the dopant depth profile. The rise and fall of the voltage pulse will not be included in the measurement and calculation, as they do not contain any critical information for implant profile calculation.
The measured IEDs from Fig. 18 for all the boron and fluorine ions implanted into the wafer were used as inputs [32] into implant-simulation software. The Stopping and Range of Ions in Matter (SRIM) simulation [33, 34] was used to compute and predict implant profiles, to which the SIMS results were compared. Since SRIM only accepts atomic ions, the BF$_x^+$ (x = 1, 2, 3) IEDs are normalized to the total ion flux and are converted into equivalent boron IED (B$_{eq}^+$) and equivalent fluorine IED (F$_{eq}^+$) by using the following formulas for each energy:

$$E(B_{eq}^+) = E(BF_x^+) \times \frac{m_B}{m_{BF_x^+}}$$ \hspace{1cm} (4.1),

$$E(F_{eq}^+) = E(BF_x^+) \times \frac{m_F}{m_{BF_x^+}}$$ \hspace{1cm} (4.2)

The results from the conversion of the ion energy distributions into boron equivalent energies are shown in Fig. 26 for each boron containing ion. The boron equivalent energy for each ion can then be used separately to estimate the impact of each ion on the final profile. They can also be combined together to give the total boron equivalent energy (B$_{eq}^{tot}$) by using the following formula:

$$E(B_{eq}^{tot}) = \sum_{x=0}^{3} E(BF_x^+)$$ \hspace{1cm} (4.3)

![Figure 26: Calculated boron equivalent energy for each boron ion, normalized to the total flux of boron ions based on 500 V 100 mTorr IEDs of the ions reaching the wafer [15]](image)

Fig. 27 shows the equivalent boron and fluorine IEDs under the previously described discharge conditions. As expected, the main part of the boron and fluorine equivalent ion energies are below 250 eV.
The equivalent boron and fluorine energies are partitioned into energy bins. Each energy bin defines an ion dose fraction of the total flux of the boron ions coming onto the wafer. The average energy of each bin is used as the input energy for the SRIM calculation. All the output depth profiles from SRIM are then linearly interpolated to obtain the predicted depth profile, based on the IEDs of all the ions striking the wafer. A calculation of a B⁺ implanted at 1 keV was performed at various angles and the results are presented in Fig. 28. It should be noted that for angles below 15°, only minor differences can be observed on the simulated profiles. In the following sections, only normal incident ions to the silicon surface will be considered.

The predicted boron and fluorine profiles were calculated using the protocol described above and were then scaled up to the SIMS measured dose. A comparison between the predicted profile and the experimental boron and fluorine SIMS profiles is shown in Fig. 29.
Figure 29: Boron and Fluorine predicted depth profiles, based on the measured ion mass and energy distributions for crystalline and pre-amorphized silicon wafer (PAI), compared with the measured SIMS depth profile for the same implant conditions (500 V 100 mTorr BF3 PLAD) [15]

When a crystalline wafer is used, a good correlation is obtained between the simulation and the experimental SIMS profiles of both elements in the shallower part of the profile, but the measured profile is deeper than the predicted one. In the boron and fluorine SIMS profiles, a typical channeling tail [15] inside the crystalline wafer can be observed. This is not reflected in the predicted profiles, because SRIM simulation assumes amorphous target. This channeling tail, obtained at 0.5 kV with a crystalline silicon wafer, confirms that the majority of the ions are reaching the wafer with a small angle (lower than 15°). When a pre-amorphized substrate (PAI) is used, there is no channeling tail and the predicted boron profile then also matches the deeper part of the measured SIMS profile for the 0.5 kV case (see “B SIMS PAI” curve on Fig. 29).

Figure 30: Contribution of each ion reaching the wafer (B+, BF+, BF2+ and BF3+) onto the boron depth profile

By doing the simulation for each ion separately for the 0.5 kV 100 mTorr PLAD, the particularities of a PLAD dopant profile (surface peak and very shallow profile) can be explained. Fig. 30 shows the role of each ion species reaching the wafer: B+ defines the depth of the implant, BF+ and BF2+ are the
main contributors to the surface dose, and BF3+ does not have any significant impact on the SIMS profile.

6. Conclusion
In this paper we have measured ion energy distributions of the ions from the sheath of the dc pulsed discharge through BF3. For conditions where the number of collisions in the sheath is minimal (< 2) the measured ion energy distributions are dominated by the high energy peak. In the collisional sheath, measured IEDs are reflecting the complexity of elastic and inelastic collisions in the sheath. The results indicate that positive ions undergo several elastic collisions, with charge exchange being a dominant inelastic collision.

We have computed ion energy distribution of the major ion for different number of collisions in the high voltage sheath. The computed number of collisions using Davis Vanderslice model overestimated this number in the collisional sheath. The experiments confirm that dissociation of the main ion species in the sheath is the most likely mechanism that explains this discrepancy. Our previous calculations [15] are in agreement with these findings.

The stopping and range of ions in matter simulation was used to predict profiles of the implanted atomic species in the silicon which the secondary ion mass spectrometry results were compared. A series of SRIM simulations, based on the spectrometric data, were performed to calculate the boron and fluorine dopant depth profiles. The calculated profiles matched very well the ones measured for different discharge parameters. The predicted profiles also provided additional explanation for the surface-peaked SIMS profile that is unique to plasma doping. This knowledge is useful to control and optimize implant profiles and dopant activation.

As with traditional ion implantation, the implant profiles can now be predicted based on the ion energy distributions measured in the high–voltage sheath. The same method can be used to optimize the dopant profile for the junction engineering. By changing the discharge parameters and by understanding the sheath dynamics device properties can be adjusted for best performance. The other big advantage is that the dopant profile can be predicted simultaneously with new device development.

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