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Energy transfer from radio frequency sheath accelerated CF$_3^+$ and Ar$^+$ ions to a Si wafer

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The thermal energy flux which a rf plasma delivers to a silicon surface has been studied by a calorimetric method. The energy flux appears to be proportional to the product of the average ion energy and the ion flux, which was calculated from the Bohm criterion using measured plasma parameters. Furthermore, the value and energy dependence of the kinetic energy transfer efficiency (about 0.5) suggests that the microscopic interaction of impinging ions in the eV range with a silicon surface can be described by a binary collision model.

Plasma-wall interactions are important to a large variety of plasma chemistry applications such as etching, deposition, and surface modification. In these processes the thermal conditions at the substrate surface play a dominant role. The surface temperature ($T_s$) influences elementary processes like adsorption, desorption, diffusion, and chemical reactions. The energy transfer from plasma to solid is a very complicated mechanism. In the case of thermal plasmas this transfer can be described by means of classical terms as thermal conductivity and heat transfer coefficient. For non-equilibrium plasmas such an approach is not possible. In those plasmas the energy is shared between translation, rotation, vibration, dissociation, and ionization. The distributions over the several energy modes, i.e., the several temperatures, depend strongly on the discharge conditions.

In the present letter we perform an experimental investigation on the energy transfer from a rf plasma to a silicon surface. The thermal probe substrate consists of three 4 in. silicon wafers, glued together with Varian Torr Seal epoxy glue. In each of the two epoxy layers three type-j thermocouples are mounted (see Fig. 1). This geometry allows us not only to study the wafer heating, but also, by comparing the temperature in the two layers of epoxy, the heat flux through the wafer. The plasma reactor has been described more extensively elsewhere. It basically consists of a closed-geometry, planar rf discharge with an electrode diameter of 10 cm. It is equipped with microwave and laser diagnostics for the determination of the density of electrons and negative ions, infrared absorption spectroscopy for the determination of the translational, rotational, and vibrational temperatures, and energy-resolved mass spectrometry for the determination of the ion energy distribution at the surface. The used gases were CF$_4$ and Ar at flow rates of 20 and 40 sccm and at pressures of 50, 100, and 350 mTorr. The 13.56 MHz rf power was 20, 40, 60, or 80 W.

Immediately after plasma ignition (close to $t=0$), the measured temperatures in the two epoxy layers are observed to be equal. Therefore conduction can be neglected in this stage. At $t=0$ the wafer is still at room temperature, so radiation and convection can also be neglected. Since there are no effective loss processes at $t=0$, the total heat influx $\dot{H}_S$ can be obtained from the initial slope of the heating curves $T_S(t)$ measured by the thermocouples. Figure 2 shows an example of $T_S(t)$. The relation between the measured initial slope ($\dot{T}_S$) and the energy flux $\dot{H}_S$ is described by energy conservation:

$$\dot{H}_S = C_S \left( \frac{\partial T_S}{\partial t} \right)_{t=0},$$

where $C_S$ is the heat capacity of the wafer.

Under our conditions, radiation heating and heating by vibrational, rotational, and translational energy transfer can be neglected: separate experiments using infrared absorption spectroscopy have shown that the several associated temperatures ($T_{\text{vib}}, T_{\text{rot}}, T_{\text{trans}}$) are nearly the same as the surface temperature $T_S$. Therefore we can restrict ourselves to the analysis of the heating of the Si surface by ion bombardment.

The energy $\dot{Q}_{\text{in}}$ supplied by the ions to the substrate consists of a potential and a kinetic contribution:

$$\dot{Q}_{\text{in}} = j A (\kappa_p E_p + \kappa_k E_k),$$

where $j$ denotes the ion fluence, $A$ the electrode area (79 cm$^2$), $E_p$ and $E_k$ the potential and kinetic energy of an impinging ion, respectively; $\kappa_p$ and $\kappa_k$ are the corresponding energy transfer coefficients. Under our discharge conditions the ion fluence $j$ is determined by the Bohm criterion which yields

$$j = n_+ \exp(-0.5) \sqrt{kT_e/m_+},$$

where $n_+$ is the ion concentration, $T_e$ the electron temperature, and $m_+$ is the mass of incident ion. The potential energy $E_p$ equals the ionization potential $E_i$; the kinetic energy $E_k$ must be measured or calculated. For the energy transfer coefficients $\kappa_p$ and $\kappa_k$ expressions are given in the literature:

$$\kappa_p = 1 - \frac{\phi}{E_i} - \gamma \frac{\phi + E_k}{E_i},$$

and
FIG. 1. Design of the thermal probe wafer structure.

\[ \kappa_e = k_e \alpha = k_e \left( A \frac{M_1 M_2}{(M_1 + M_2)^2} \sin \theta / 2 \right)^2 \]

where \( M_1, M_2 \) are the atomic masses of the colliding particles, \( \theta \) is the angle of incidence of the ions, and \( k_e \) is the kinetic energy transfer efficiency. The transfer mechanism of the potential energy takes into account the neutralization of the ion by a released electron, which is described by the work function \( \phi \). Under these plasma conditions, the thickness of the modified surface layer (Si,C,F,) is very small (monolayer), so the work function of the silicon bulk has to be taken. In addition a secondary electron can be ejected (with probability \( \gamma \)), which consumes a small part of the energy. The kinetic transfer coefficient \( \kappa_e \) is a product of the internal conversion coefficient \( \alpha \) and the kinetic energy transfer efficiency \( k_e \), which is related to the number of individual collisions an impinging ion has with atoms in the solid state.

The interpretation of the substrate heating by ion bombardment requires the knowledge of \( E_k, n_+, \) and \( T_e \). The mean kinetic energy \( E_k \) was determined by means of energy resolved mass spectrometry. The dominant ion in CF$_4$ discharges was found to be CF$_3^+$. Microwave resonance spectroscopy in combination with laser-induced photodetachment has supplied the electron and negative ion density data. The axial profile of the negative ion density shows that they are not present in the sheath or presheath: the density only builds up in the glow. Therefore, in order to calculate the ion fluence \( j \) from the Bohm criterion, the required positive ion density at the sheath boundary \( n_+ \) can be taken to be equal to the electron density. The electron temperature was estimated

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>( n_+ ) (cm$^{-3}$)</th>
<th>( E_k ) (eV)</th>
<th>( \langle \partial T_e / \partial t \rangle = 0 ) (K/s)</th>
<th>( j ) (cm$^{-2}$ s$^{-1}$)</th>
<th>( j_{\alpha E_k A} ) (J/s)</th>
<th>( j_{\kappa_e E_k A} ) (J/s)</th>
<th>( \dot{H}_S ) (J/s)</th>
<th>( k_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_4$, 20 sccm 50 mTorr 20 W</td>
<td>6.2x10$^9$</td>
<td>42</td>
<td>2.0x10$^{-3}$</td>
<td>7.6x10$^{14}$</td>
<td>0.035</td>
<td>0.17</td>
<td>0.114</td>
<td>0.46</td>
</tr>
<tr>
<td>CF$_4$, 20 sccm 100 mTorr 20 W</td>
<td>5.1x10$^9$</td>
<td>40</td>
<td>2.1x10$^{-3}$</td>
<td>6.2x10$^{14}$</td>
<td>0.029</td>
<td>0.13</td>
<td>0.120</td>
<td>0.70</td>
</tr>
<tr>
<td>CF$_4$, 20 sccm 100 mTorr 40 W</td>
<td>8.2x10$^9$</td>
<td>52</td>
<td>3.8x10$^{-3}$</td>
<td>10.0x10$^{14}$</td>
<td>0.044</td>
<td>0.27</td>
<td>0.217</td>
<td>0.63</td>
</tr>
<tr>
<td>CF$_4$, 20 sccm 100 mTorr 60 W</td>
<td>13.2x10$^9$</td>
<td>57</td>
<td>5.6x10$^{-3}$</td>
<td>15.9x10$^{14}$</td>
<td>0.067</td>
<td>0.48</td>
<td>0.320</td>
<td>0.52</td>
</tr>
<tr>
<td>CF$_4$, 20 sccm 100 mTorr 80 W</td>
<td>19.1x10$^9$</td>
<td>65</td>
<td>8.5x10$^{-3}$</td>
<td>23.2x10$^{14}$</td>
<td>0.093</td>
<td>0.80</td>
<td>0.486</td>
<td>0.49</td>
</tr>
<tr>
<td>Ar, 40 sccm 350 mTorr 20 W</td>
<td>1.8x10$^9$</td>
<td>15</td>
<td>1.1x10$^{-3}$</td>
<td>2.8x10$^{14}$</td>
<td>0.036</td>
<td>0.022</td>
<td>0.063</td>
<td>1.22</td>
</tr>
</tbody>
</table>

FIG. 2. An example of the evolution of the substrate temperature as a function of time induced by plasma ion bombardment.
FIG. 3. The energy needed to heat the probe wafer ($H_s$) as a function of the kinetic energy which the plasma offers to the surface. The horizontal axis has been corrected for the influence of the mass of the impinging ion [see Eq. (5)].

from attachment rate measurements, and confirmed by calculations of the plasma chemistry.\textsuperscript{10} The required values for $E_i$, $\phi$, and $\gamma$ were taken from the literature.\textsuperscript{13,16} For the calculation of $a_j E_k$ we assumed an angle of incidence $\theta = 90^\circ$. The kinetic energy transfer efficiency $k_e$ is not known a priori, and is determined from this work. To obtain the heat influx $H_s$ by measurement of $(\partial T_s/\partial t)_{t=0}$ we need the heat capacity of the sandwich wafer device, which was determined calorimetrically ($C_s = 57 \text{ J/K}$).

In Table I all experimental conditions and derived physical quantities are summarized. In Fig. 3, which can be extracted from Table I, the calculated value $j a E_k A$, which is equivalent to the (uncorrected) kinetic energy transfer from ions to surface, is plotted versus the energy $H_s$ absorbed by the wafer (measured by the thermocouples). The relation appears to be roughly linear. Because of the transfer of potential (=ionization) energy to the surface [cf. Eqs. (2) and (4)] the line does not pass through zero. What we can learn from Fig. 3 is that the heating of a silicon wafer is proportional to the energy fluence (energy times number density times Bohm velocity) of the ion bombardment.

Another result which can be drawn from Table I is the kinetic energy transfer efficiency $k_e$ [see Eq. (5)]

$$k_e = \frac{H_s - j k_p E_p A}{j a E_k A}.$$  \hspace{1cm} (G)

In Fig. 4, $k_e$ is plotted as a function of the average energy of the ion bombardment. The value of $k_e$ ranges around 0.5, with a tendency to increase for lower energies. This is in perfect agreement with data reported by Winters\textsuperscript{3} for the low energy regime, be it that Winters' data are taken for the energy transfer from noble gas ions to a tungsten surface. Winters has also shown that under conditions where there is little lattice penetration a binary-collision model yields predictions of $k_e$ which reproduce the experimental results very well.

We would like to conclude that the heating of a silicon wafer due to exposure to a rf CF$_4$ plasma is primarily caused by the bombardment with CF$_3^+$ ions. The energy transfer is described very well by the binary-collision model, which agrees with the findings of Winters.\textsuperscript{3}

This study was made possible by support from the NATO Scientific and Environmental Affairs Division under Grant No. CRG 910895.

\textsuperscript{13}B. Chapman, Glow Discharge Processes (Wiley, New York, 1980).
\textsuperscript{16}Handbook of Chemistry and Physics, 57th ed., edited by R. C. Weast (Chemical Rubber, Cleveland, OH, 1976).