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Selective Control of Chemical Reactions With Plasmas

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SUMMARY

With the growing applications in the semiconductor and communication industries of multi-component materials, such as III-V semiconductors, low-k and high-k materials, and SiGe,\textsuperscript{1-4} the control of selectivity when these materials are etched using plasmas is important. The preferential etching of one component of a multi-component material surface degrades the surface and increases the surface roughness.\textsuperscript{5-7} Control of the reaction selectivity on the substrate surface during plasma etching is determined by the concentration of reactive species generated in the bulk plasma and by the interaction of the ions and neutrals in the plasma with the substrate surface. This research work focused on control of the reactive species inside a plasma through measurement and manipulation of the electron energy distribution function (EEDF) and on understanding the surface reaction mechanisms on the substrate exposed to a combination of ion and atom beam sources to simulate a real plasma. The grant proposal was titled “Selective Control of Chemical Reactions with Plasmas,” (DE-FG03-00ER54581) with a project period of August 15, 2000 through August 14, 2003, which was extended to January 31, 2004, for a total award amount of $195,000.

A GEC chamber (Gaseous Electronic Conference Reference Cell)\textsuperscript{8} with a mass spectrometer and a Langmuir probe (LP) system were used for this research. It was found that H\textsubscript{2} and N\textsubscript{2} additives to an Ar plasma could effectively change the EEDF and the average electron temperature ($T_e$). This finding provides the possibility to selectively control reaction rates in the plasma to control etching selectivity on a surface. This concept was demonstrated in Ar/N\textsubscript{2}/H\textsubscript{2} and Ar/CH\textsubscript{4}/H\textsubscript{2} systems.

A beam reactor with independent ion and atom beam sources was set up to explore the reaction chemistry on a substrate. The combination of ion and atom beam sources provides the
ability to simulate a plasma and decouple the complicated chemistry to simplify the problem.
InP, SiGe, MSQ (methylsilsesquioxane) were chosen for study because of their multi-component properties and important applications.

**ACCOMPLISHMENTS**

- Reproduced literature results for Ar in capacitive mode plasma. Calibrated Langmuir Probe with GEC system at powers from 50-200 W and pressures from 50-200 mTorr.

- Modified GEC system to operate in inductive mode. Calibrated Langmuir Probe in this ICP system at powers from 10-140 W and pressures from 1-21 Pa.

- Explored the effect of gas (H₂, D₂, N₂) addition to affect the EEDF and Tₑ in the GEC system in capacitive mode at powers from 50-150 W and pressures from 50-100 mTorr.

- Demonstrated proof of concept for control of reaction selectivity by changing EEDF with gas addition for Ar/CH₄/H₂ and Ar/N₂/H₂ systems. H₂ addition increased the Tₑ of Ar/CH₄/H₂ plasma.

- Set up a beam reactor to explore chemical reaction mechanisms at the plasma substrate interface by the simulation of a plasma using ion and atom beam sources. The ion and atom beam source calibration was completed and the surface modification by Ar ion bombardment was tested for MSQ and InP. Etching rates between 2 to 380 nm/min were achieved for MSQ using Ar ions with energies from 100 to 1000 V at room temperature.
EXPERIMENTAL

A GEC chamber (Gas Electronic Conference Reference Cell) was used for the measurement of plasma properties and for exploring the control of EEDF (electron energy distribution function). For convenience in comparing to a Maxwellian distribution, EEPF (electron energy probability function) was measured and used for presenting the results and discussion. The relationship between EEDF \( F(\varepsilon) \) and EEPF \( f(\varepsilon) \) is defined as \( F(\varepsilon) = \varepsilon^{1/2} f(\varepsilon) \), where \( \varepsilon = V - V_p \). A Langmuir probe system (SmartProbe, Scientific Systems Inc.) was purchased and used for the measurement of plasma I-V curves. The probe software calculates the parameters electron density \( N_e \), ion density \( N_i \), electron temperature \( T_e \), floating potential \( V_f \), plasma potential \( V_p \) and EEPF. This probe system has been widely used in the plasma research community. The parameters were measured for powers up to 200 W and pressures up to 200 mTorr. The probe location was controlled through a XYZ manipulator. In most experiments, the probe tip was fixed horizontally at the center of the electrode and vertically 1 cm from the top electrode.

A MKS mass spectrometer system was used for the GEC system to monitor the plasma. A Labview controlled gas-handling system was setup to provide independent control of multiple inlet gases. A manual matching network was used for maintaining the reflected power to below 5%. A Bird power meter was used to monitor the inline power.

The GEC was modified to an ICP system. In the inductive mode the top electrode was replaced with a glass window. A manual matching network with an antenna system was put on the top of the window to inductively couple the power into the chamber. The same probe system
was used to measure the Ar plasma parameters at powers from 10-140 W and pressures from 1-21 Pa.

A beam reactor was setup to investigate plasma-substrate reaction mechanisms.13-15 A manipulator provided XYZ rotation and angle tilt ability to the sample holder. With further modification, it could provide temperature control for TPD (temperature programmed desorption) research. One ion beam source (RF25) and one atom beam source (HD25) from Oxford Applied Research Inc. were purchased to simulate the plasma. An OED (optical emission detector) system from the same company was purchased for the calibration of the atom beam source. The OED system gave the voltage reading through the measurement of emission intensity by a Si detector. The system measures the desired wavelength emission intensity using filters. By choosing one typical emission wavelength for the gas in the atom beam source, the OED system gave the relative atom flux through the voltage reading. A FC (faraday cup) system from Kimball Physics provided the ability to calibrate the ion beam source. A Balzers QMG420 mass spectrometer system was attached to monitor the background gas in the system.

The ion beam source was calibrated by a FC system. The flux change with source power and source screen voltage was measured. The ion energy distribution was measured when a sweeping voltage was exerted on the FC system. The measured current varied from $20 \times 10^{-6}$ A at a screen voltage of 300 V to $95 \times 10^{-6}$ A at 1000 V. The atom beam source was calibrated using the OED system to measure the relative flux at different source powers and gas flow rates.

The research group also has surface analysis capabilities including XPS, FTIR and AFM analysis of samples.
RESULTS

Ar plasma parameters were measured in both capacitive and inductive mode for different powers and pressures. The measured data served as a baseline to compare the performance of the chamber and probe to literature results and as a monitor of conditions after processing with more complicated chemistries. The measurement also provided general understanding of process parameters such as power and pressure in affecting plasma parameters.

H₂ and N₂ were added to Ar plasmas to try to exert control over reaction selectivity by changing the EEPF. H₂ and N₂ were selected because they have very different electron excitation cross-sections. The experiments demonstrated that effective control of EEPF was possible by gas addition. Ar/CH₄/H₂ and Ar/N₂/H₂ plasmas were used to apply the concept of selectivity control.

Ar Capacitively Coupled Plasma

Figure 1 shows the Te change with power at 50, 100, 150 and 200 W, and pressure at 50, 100, 150 and 200 mTorr. For a fixed pressure, the Te dropped with an increase in power. For a fixed power, the Te dropped with an increase in pressure. The largest drop in Te occurred between 50 and 100 mTorr for all four powers studied. Above this range, the Te decreased more slowly. Lower pressures provide higher Te due to a reduced collision frequency between electrons and the background gas. The higher power reduces Te at the same pressure since higher power increases electron density further reducing the Te by increasing collisions between electrons and electrons and electrons and neutrals. The Te was also affected by the change in heating mode, which is a function of power and pressure in the GEC system.

Figure 2 shows the change of Ne and Ni for different powers from 50-200 W and pressures from 50-200 mTorr. It shows that for a fixed pressure, Ne and Ni increased almost linearly with power as in the literature. At higher pressure, Ne and Ni increased faster with power change compared to lower pressure. For example, for 50 mTorr, the Ne increased from
$1.7 \times 10^{10} \text{ cm}^{-3}$ to $3.5 \times 10^{10} \text{ cm}^{-3}$, but for 200 mTorr, the $N_e$ increased from $7.1 \times 10^{10} \text{ cm}^{-3}$ to $1.9 \times 10^{11} \text{ cm}^{-3}$ from 50 W to 200 W. The reason is that for the same power, higher pressure provides a higher collision frequency so it is more efficient in producing electrons and ions as long as the incident electron energy is above ionization threshold energy during the collision.

Figure 3 shows the EEPF change with pressure at 100 W net input power. At 50 mTorr two linear regions were obtained with a break point at 5 eV, which indicates a bi-Maxwellian electron energy distribution. With increased pressure, the two linear regions gradually merged into one indicating a change from a bi-Maxwellian distribution to a Druyvesteyn distribution. The change of EEPF from a bi-Maxwellian distribution to a Druyvesteyn distribution with increased pressure is a well-recognized phenomenon in capacitively coupled plasmas.\textsuperscript{20-22}

Measurements on Ar capacitively coupled plasmas were made at regular intervals to monitor the chamber condition.

**Ar Inductively Coupled Plasma**

In inductive mode the ion and electron densities are much higher at a given power than in a capacitively coupled plasma (Figure 4). For example, at 21 Pa and a power of 20-30 W, $N_e$ increased from $9 \times 10^9 \text{ cm}^{-3}$ to $5 \times 10^{10} \text{ cm}^{-3}$. This feature is caused by a transition in the heating mode at the critical power, which is a function of pressure. Once the critical power was reached, the plasma changed from capacitive mode to inductive mode with a clearly observed light intensity change. Once the system reached inductive mode, $N_e$ and $N_i$ became relatively stable with an increase in power. Compared with capacitive mode, the density of $N_e$ and $N_i$ were generally an order of magnitude higher in inductive mode\textsuperscript{11,23} but with a lower $T_e$. 
H₂ Addition in Changing Plasma Properties

H₂ was added to an Ar plasma in capacitive mode, the change of plasma properties with H₂ was measured by the probe system. Figure 5 shows that H₂ addition to 23% at 50, 100 and 150 W and at 50, 100 mTorr changed the Tₑ by a factor of two or more.

As a comparison, D₂ was added to an Ar plasma. Figure 6 shows that D₂ addition produced the same trend in Tₑ as H₂ addition. As a comparison, the 100 W, 100 mTorr H₂ addition data are plotted in Figure 6. This shows that the Tₑ is very close in the two systems.

Figure 7 shows the changes in EEPF with H₂ addition at 100 W and 100 mTorr. From this figure H₂ addition produced a bi-Maxwellian distribution as shown by the change in slope at an electron energy of approximately 5 eV. Moreover, the high-energy tail of the EEPF shifted up with increasing H₂ concentration, which means that the high-energy electron population increased with pressure. This result is incorporated into Tₑ as a higher average electron temperature but shows that the details of the EEPF are important to control of the energy distribution of electrons and ultimately electron induced chemical reactions.

N₂ Addition in Changing Plasma Properties

The addition of N₂ to an Ar capacitive plasma caused a different change in the plasma properties than H₂ addition. Figure 8 shows that the system was very sensitive to N₂ concentration,²⁴ as a small amount of N₂ (<3%) added into the system caused an almost 50% drop in Tₑ from the original value in pure Ar. Above 3% N₂ addition, however, the Tₑ remained relatively stable with further increases in the N₂ concentration. Compared with the heating effect in an Ar plasma by H₂ addition, the N₂ addition provided a cooling effect to the electrons.

Figure 9 shows the EEPF change with N₂ addition at 100 W, 100 mTorr. It shows that the EEPF of the system maintains the bi-Maxwellian structure of the Ar plasma. However, compared
with pure Ar, the EEPF has a deep shoulder near 4 eV, which has been observed by other researchers.\(^{22,25}\) Above 3% N\(_2\), a further increase of N\(_2\) concentration didn’t cause obvious change in the shape of the EEPF.

**Addition of H\(_2\) and N\(_2\) to Control the Electron Energy Distribution in a Plasma**

The results of H\(_2\) and N\(_2\) addition separately provide a heating and cooling method for electrons in Ar plasmas and both change the EEPF. The combination of H\(_2\), N\(_2\), and Ar is used commonly in industrial applications and has been explored by several researchers.\(^{26-29}\) In this work the combination of H\(_2\) and N\(_2\) shows that the \(T_e\) is dominated by the presence of N\(_2\) (Figure 10). The \(T_e\) in an Ar/3% N\(_2\) plasma was relatively stable with increasing H\(_2\) concentration. \(T_e\) values were close to the Ar/N\(_2\) system (Figure 8). Moreover, with an increase in the concentration of H\(_2\) in the system, \(T_e\) decreased slightly. The Ar/N\(_2\)/D\(_2\) system displayed similar behavior.\(^{30}\)

Methane based plasmas are widely applied in industry for coating and deposition technologies.\(^{31,32}\) Ar/CH\(_4\)/H\(_2\)\(^{33,34}\) and CH\(_4\)/H\(_2\)\(^{35,36}\) systems are commonly used for the etching of InP. H\(_2\) has been added to an Ar/CH\(_4\) system and the \(T_e\) was measured. Figure 11 shows that at CH\(_4\) 2.2%, 50 mTorr, and applied powers of 50, 100 and 150 W, the \(T_e\) increased with an increase in the H\(_2\) concentration. At 50 W, 50 mTorr, \(T_e\) increased from 2.8 eV to 4.7 eV. To demonstrate the affect of a change in \(T_e\) on the plasma chemistry, a calculation of CH\(_4\), CH\(_3\), CH\(_2\) ionization and dissociation rates was done assuming a Maxwellian electron energy distribution (Figure 12). It shows that below 4 eV the system is CH\(_x\) dissociation dominant and above 4 eV it is ionization dominant.
Discussion of the Gas Addition Effect

The reason for the change of $T_e$ and EEPF with H$_2$ and N$_2$ addition could be partly explained by the difference in excitation cross-section. For a fixed net input power, the power absorbed by the plasma is constant. However, energy losses in collision processes will be modified by H$_2$ and N$_2$ addition. The energy loss in the system by electron collisions with neutrals could result in excitations and ionizations, or simply elastic collisions.$^{37,38}$ Excitation and ionization require incident electrons to lose energy. However, the cross sections of Ar, N$_2$, and H$_2$ produce different collision frequencies and a concomitant change in the behavior of the system with $T_e$. Figure 13 shows that the N$_2$ excitation cross section has a sharp peak near 3 eV.$^{39-41}$ The EEPF of Ar/N$_2$ shows that the sharp peak in the cross section is related to the decrease in $T_e$. Due to enhanced excitation reactions inside the plasma by N$_2$ addition, the N$_2$ acts as a sink for energetic electrons and quenches the plasma through excitation collision energy losses. Compared with N$_2$, the H$_2$ cross section in this energy range is much lower and so no quenching effect is observed for H$_2$ addition.

Figure 14 shows that the total ionization cross sections for H$_2$ and D$_2$ are much lower than for Ar over a broad energy range.$^{39}$ Since the ionization threshold energies are close for these three gases, this implies that there are fewer energy loss mechanisms for ionization in Ar/H$_2$ plasmas compared to a pure Ar plasma. The similar cross-sections for H$_2$ and D$_2$ explains the similar trends in $T_e$ with concentration.

Ion Beam Calibration

The ion beam source was calibrated by a FC (faraday cup) system. With a sweeping voltage on the FC retarding grid, this system serves as an ion energy distribution analyzer. Figure 15 shows the change of energy distribution with different source screen voltages at 200 W source
power and Ar flow rate 10 sccm. The incident ion energy distribution was relatively uniform and with a cut off once the retarding voltage was higher than the source screen voltage. The calibration shows that an increased source power and reduced source head to FC head distance increase the incident ion flux.

Figure 16 shows the ion flux change with source power and screen voltage. It shows that the ion flux changed from $0.5 \times 10^{-6}$ A at 50 V screen voltage to $96 \times 10^{-6}$ A at 1000 V screen voltage at 200 W source power. For different source powers, the ion flux was approximately the same for screen voltages below 300 V and gradually increased to a steady value above 300 V.

**Atom Beam Calibration**

The atom beam calibration was done using an OED (Optical Emission Detector) system for different source powers and H$_2$ gas flow rates. Figure 17 shows that a voltage jump occurred at a source power 100 W. This indicates that the operation mode changed from capacitive to inductive mode. Above a source power of 350 W, the detector was saturated by plasma light and no further voltage increase could be read even though the light intensity of the plasma increased with the increasing source power.

Figure 18 shows the voltage change with H$_2$ flow rate at a source power of 200 W. A maximum voltage was reached at a flow rate of 2 sccm. The voltage increased with increasing flow rate below 2 sccm and decreased with increasing flow rate above 2 sccm. Since the voltage reflects the relative atom flux, it shows that for a set power, an optimum flow rate exists for reaching the maximum atom flux.
Ar Ion Sputtering for InP

An InP wafer was sputtered using Ar ions at a source power of 200 W, Ar flow rate of 10 sccm and a screen voltage of 500 V for 30 minutes. The XPS analysis results shown in Figures 19 and 20 are the In 3d and P 2p peak spectra, respectively, before and after Ar ion sputtering. A shift to lower binding energy was obtained for the In 3d peak, which suggests that an oxide film may have been removed from the surface. The P 2p spectra, however, do not show a shift, only a decrease in intensity after sputtering.

Ar Ion Sputtering for MSQ

MSQ samples were sputtered by Ar ions at a 200 W source power, Ar flow rate of 10 sccm and screen voltages 100-1000 V for 0.5-30 minutes. Figure 21 shows the MSQ FTIR spectrum after sputtering with screen voltage 500-1000V. Ar ion sputtering reduced the CH$_3$ asymmetric and symmetric stretches. This implies that the energetic incident ions could cause preferential etching of the MSQ surface. Figure 22 shows the etching rate change with screen voltage. It shows that etching rate increased nonlinearly with screen voltage. The etching rate at a screen voltage of 100 V was 2 nm/min, but increasing the voltage increased the etching rate, which reached 380 nm/min and appeared to be leveling off at a screen voltage of 1000 V.

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Figure 1. Ar plasma $T_e$ change with power and pressure in capacitive mode

Figure 2. Ar plasma $N_e$ $N_i$ change with power and pressure in capacitive mode
Figure 3. Ar plasma EEPF change with pressure at 100 W capacitive mode

Figure 4. Ar plasma $N_e, N_i$ change with pressure and power inductive mode
Figure 5. $T_e$ change with $H_2$ concentration with power and pressure

Figure 6. $T_e$ change with $D_2$ and $H_2$ concentration with power and pressure
Figure 7. EEPF change with H₂ concentration at 100 W 100 mTorr

Figure 8. Tₑ change with N₂ concentration with power and pressure
Figure 9. EEPF change with N₂ concentration at 100 W 100 mTorr

Figure 10. T_e change with H₂ concentration at Ar/N₂/H₂ plasma with power and pressure, 3% N₂
Figure 11. $T_e$ change with H$_2$ concentration with power and pressure, 2.2%CH$_4$

Figure 12. $T_e$ effect on CH$_x$ ionization and dissociation
Figure 13. Comparison of excitation cross section. Data reproduced from reference 39,40,41.

Figure 14. Comparison of total ionization cross section. Data reproduced from reference 39.
Figure 15. Ion beam source ion energy distribution calibration, source power 200 W, Ar 10 sccm

Figure 16. Ion beam source ion flux calibration with different power and screen voltage, Ar 10 sccm
Figure 17. Atom beam source atom flux calibration with source power

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Figure 19. In 3d peak change pre and post Ar sputtering, ion energy 500V, source power 200 W, Ar flow rate 10 sccm

Figure 20. P 2p peak change pre and post Ar sputtering, ion energy 500V, source power 200 W, Ar flow rate 10 sccm
Figure 21. MSQ FTIR spectrum change pre and post Ar sputtering, ion energy 800V, source power 200 W, Ar flow rate 10 sccm

Figure 22. MSQ FTIR spectrum post-pre Ar sputtering, ion energy 800V, source power 200 W, Ar flow rate 10 sccm