APPLIED PHYSICS LETTERS **88**, 151502 (2006)

Fluorine negative ion density measurement in a dual frequency capacitive plasma etch reactor by cavity ring-down spectroscopy

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(Received 12 December 2005; accepted 28 February 2006; published online 12 April 2006)

F^- negative ions were detected by direct observation of the weak photodetachment absorption continuum below 364.5 nm by cavity ring-down spectroscopy. The negative ions were generated in a modified industrial dielectric plasma etch reactor, with 2+27 MHz dual frequency capacitive excitation in $Ar/CF_4/O_2$ and $Ar/C_4F_8/O_2$ gas mixtures. The F^- signal was superimposed on an unidentified absorption continuum, which was diminished by O_2 addition. The F^- densities were in the range of $(0.5-3)\times 10^{11}$ cm^{-3}, and were not significantly different for single (27 MHz) or dual (2+27 MHz) frequency excitation, not confirming recent modeling predictions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2194823]

SiO_2-based dielectric films are etched in the industrial fabrication of integrated circuits using low pressure radio-frequency excited plasmas containing fluorocarbon precursors such as CF_4 and C_4F_8.[1] These gases, and also probably their decomposition products, can undergo dissociative attachment processes leading to the creation of F^- negative ions. Negative ions can have a significant effect on the plasma, changing the electrostatic structure of the discharge and the charged particle transport, and participating in rapid ion-neutral and ion-ion reactions. Furthermore, if they can reach the etched substrate, they may play an important role in mitigating profile charging effects that can otherwise cause problematic deviations from perfectly vertical etch profiles.[2]

F^- ions have previously been detected by laser photodetachment, followed by detection of the photoelectrons by Langmuir probe or microwave resonator techniques.[3–6] However, these techniques are difficult to implement in the chemically and electrically aggressive environment of an industrial etch reactor and may cause perturbations. Furthermore, they give results that are difficult to put on an absolute scale. Measurement of the optical absorption below the photodetachment threshold gives a direct measurement of their absolute density, and avoids inserting probe devices into the plasma, but has previously only been achieved for very high F^- densities[7] due to the small cross section. Cavity ring-down spectroscopy allows very small absorbances to be measured, and has been used to detect H^- (Refs. 8 and 9) and O^- (Ref. 9) negative ions in the visible spectral region where excellent mirrors are available. However, the detection of F^- ions is more challenging as the mirrors available at the necessary short wavelengths have much poorer overall reflectivities.

Dual frequency capacitively coupled plasma excitation is widely used for industrial dielectric etching, as it allows the generation and control of medium to high plasma densities (10^{10} to above 10^{11} cm^{-3}) with reasonably independent control of the mean energy of positive ions striking the substrate. Our plasma reactor is based on an industrial tool, excited at 2+27 MHz and using typical high-aspect-ratio contact (HARC) etch chemistries of Ar ($\approx$90%)$/C_4F_8/O_2$. In some experiments the C_4F_8 was replaced by CF_4.

Recent particle-in-cell (PIC) simulations by Georgieva *et al.*[10] have predicted that F^- ions should be electrostatically confined in 27 MHz single frequency plasmas (reaching densities in the range 10^{11} cm^{-3}), but when a 2 MHz component is added the F^- ions would be expelled. One of the aims of this work was to test this prediction.

The experimental setup is shown in Fig. 1. The plasma was formed in a modified commercial dual frequency capacitively coupled dielectric etch reactor, designed for 200 mm industrial wafer processing using fluorocarbon gases. The capacitive discharge is driven between two electrodes spaced by 25 mm. The upper (silicon) electrode is grounded. rf power at frequencies of 2 and 27 MHz is supplied to the lower electrode, which is covered by a (unclamped) 200 mm silicon wafer. The plasma is confined radially by a stack of five quartz rings spaced by several millimeters. Gases used in this study were Ar, CF_4, C_4F_8, and O_2 which enter through a showerhead in the upper electrode and exit through the gaps in the confinement rings before being pumped out of the reactor. The gas pressure inside the rings was typically around 50 mTorr with input powers of 250 W for the single frequency case and 500 W for dual frequency (2 MHz =250 W; 27 MHz=500 W).

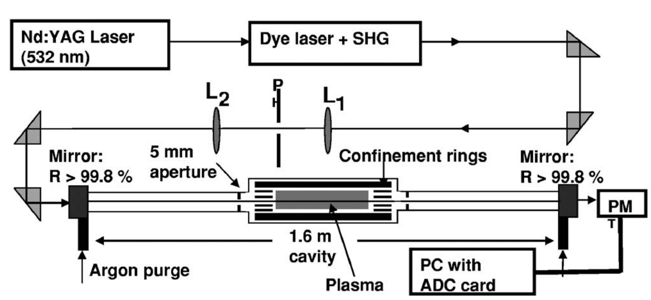

FIG. 1. Schematic of the experimental setup.

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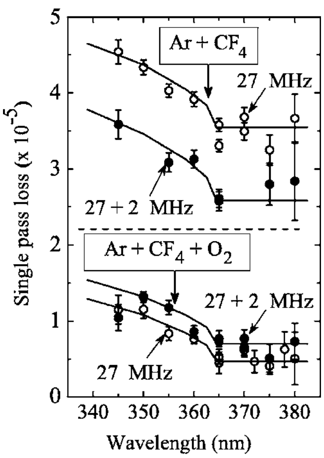

FIG. 2. The single pass loss as a function of laser wavelength for Ar/CF_4 (160/36 SCCM) and $Ar/CF_4/O_2$ (160/36/8 SCCM) single (HF=250 W) and dual frequency (HF=250 W, LF=250 W) discharges at 48 mTorr. The estimated F^- densities are 1.2×10^{11} cm^{-3} (Ar/CF_4) and 0.9×10^{11} cm^{-3} ($Ar/CF_4/O_2$), irrespective of the presence of 2 MHz power.

Cavity ring-down spectroscopy was used to measure the absorption spectrum of the plasma. The optical cavity consisted of two high reflectivity mirrors (Layertec, $R>99.8\%$ in the 340–380 nm range), 1 m radius of curvature mounted 1.6 m apart on flexible bellows at the end of extension tubes. An argon gas purge was injected close to the mirrors, and 5 mm diameter apertures were installed between the extension tubes and the chamber in order to prevent reactive species from the plasma from reaching the mirror surfaces.

The laser beam was produced by a frequency-doubled Nd-YAG (yttrium aluminum garnet) (532 nm at 10 Hz) pumped dye laser (Sirah, using either Styryl 8 or Pyridine 2 dyes) with frequency doubling. Typical laser energies were several tenths of a millijoule in the range of 340–380 nm, with a pulse duration of 9 ns. The laser beam was directed into the optical cavity and through the reactor at midheight. The laser beam quality was improved by a spatial filter consisting of a 50 mm focal length lens (L_1) and a 50 μm pinhole (PH), and then injected into the cavity with a 60 mm focal length lens (L_2). This improved the spectrum reproducibility and base line stability. The light exiting the opposite end of the cavity was detected by a photomultiplier tube (Hamamatsu R3896) fitted with an UV bandpass filter (Schott DUG 11X) to exclude visible light. The exiting light is observed to decay exponentially with a time constant known as the ring-down time τ:

$$\tau(\lambda)=\frac{L}{c[1-R(\lambda)]}, \tag{1}$$

where L is the cavity length, c is the speed of light, and R is the mirror reflectivity. When an absorbing medium is added, the ring-down time of the cavity is reduced. The ring-down signal was passed through a 500 ns *RC* filter and digitized on a personal computer using a 14-bit vertical resolution fast data acquisition card (Gage Compuscope 14200), using a 200 ns sampling interval with 160 points per laser shot (i.e., 32 μs overall sample length). A LABVIEW™ routine was developed to control the data acquisition sequence and determine the ring-down time for each laser shot in real time. The ring-down time was calculated by fitting an exponential decay (with base line offset) using a weighted least-squares fitting algorithm. Depending on the laser wavelength, typical ring-down times between 2 and 4 μs were obtained. The plasma was switched on for 5 s and switched off for 5 s and the ring-down times for both "plasma on" and "plasma off" were calculated for 30 on/off cycles. In this way the noise could be reduced to the equivalent of 10^{-6} per single pass. The absorption (per single pass) of the plasma as a function of wavelength, $A(\lambda)$, was calculated from the difference in ring-down times for both plasma on, τ_{on}, and plasma off, τ_{off},

$$A(\lambda)=\frac{L}{c}\left[\frac{1}{\tau_{on}(\lambda)}-\frac{1}{\tau_{off}(\lambda)}\right]. \tag{2}$$

Figure 2 shows the single pass absorption as a function of laser wavelength for plasmas in Ar/CF_4 (160/36 SCCM) and $Ar/CF_4/O_2$ (160/36/8 SCCM) mixtures at 48 mTorr for 250 W single frequency (27 MHz) and for 250 W (27 MHz)+250 W (2 MHz) dual frequency (SCCM denotes cubic centimeter per minute at STP). The error bars shown represent the statistical uncertainty in the mean value of the absorbance determined at each point due to variations in the ring-down time, and do not include any estimation of systematic errors. This error is largest at the wavelength extrema, where the mirror reflectivities are lowest. Firstly we note the presence of a significant continuum absorption across the wavelength range studied, particularly when there is no oxygen present. However, there is a clear increase in the absorption for wavelengths below 364.5 nm, which can be attributed to photodetachment of F^-, and above this wavelength the base line appears to be constant. The F^- density was estimated by fitting the observed absorption spectrum to the function

$$A'(\lambda)=\sigma(\lambda)n_{F^-}L+B, \tag{3}$$

where $\sigma(\lambda)$ is the F^- photodetachment cross section at a given wavelength,[11] n_{F^-} is the F^- density, L is the plasma length, and B is a constant background. For 250 W single frequency (27 MHz), the F^- densities were estimated to be 9×10^{10} and 1.2×10^{11} cm^{-3} for the $Ar/CF_4/O_2$ and Ar/CF_4 discharges, respectively. The major source of uncertainty in these measurements is due to long-term drift in the intensity of the background absorption (and possibly in the negative ion density itself), even though we attempted to ensure that steady-state conditions were attained before taking data. Each time the wavelength is changed the optical alignment must be optimized manually, so that recording each spectrum takes about 1 h. As a result, we estimate the relative uncertainty in the negative ion density to be about ±30%. These negative ion densities are in good agreement with previous observations.[3–6,12] When low frequency power (2 MHz, 250 W) was added to the 27 MHz the F^- negative ion density was not appreciably decreased. This appears to contradict the prediction of Georgieva *et al.*[10] that in the presence of the low frequency (2 MHz), the relatively light F^- ions would be accelerated toward the electrode by the strong electric fields, whereas heavier CF_3^- ions would not respond less to the low frequency fields and become the main negative ion. However, more recent calculations,[13] taking into account our geometry and gas pressure, suggest that significant F^- deconfinement should not occur until a higher 2 MHz power than used here is applied. We are currently working to test this prediction.

Figure 3 shows the F^- absorption profile versus laser wavelength for a dual frequency $Ar/C_4F_8/O_2$

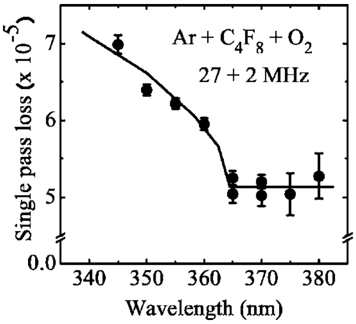

FIG. 3. The single pass loss as a function of laser wavelength for an $Ar/C_4F_8/O_2$ (160/18/8 SCCM) dual frequency (HF=250 W, LF=250 W) discharge at 48 mTorr. The estimated F^- density is 2.2×10^{11} cm^{-3}.

(160/18/8 SCCM) discharge. The other operating conditions are the same as for the CF_4 dual frequency case. With C_4F_8 the background continuum is further increased. Again, above the photodetachment threshold of 364.5 nm the base line is flat, indicating that the increase in absorption below this value is due to F^-. A fit to the experimental data shows a F^- density of 2.2×10^{11} cm^{-3}. This is two times higher than for the $Ar/CF_4/O_2$ discharge, an indication that C_4F_8 is more electronegative than CF_4.

The origin of the background continuum is not clear. It was found to increase with CF_4 concentration (and was higher with C_4F_8). The addition of oxygen to an Ar/CF_4 discharge (Fig. 2) caused the continuum absorption to decrease from $\sim 8\times10^{-5}$ to 0.5×10^{-5} (27 MHz only), while the F^- density also decreased by a factor of about 1.5. The continuum absorption may be due to other negative ions such as CF_3^- or larger carbon-containing molecules, such as C_2F. Lin and Overzet[14] observed CF_3^- ions by mass spectrometry in a pulsed inductively coupled CF_4 discharge, and found that the ions disappeared when small amounts of oxygen were added. Another possibility is the formation of dust particles in the discharge. It should be noted that when operating with an Ar/O_2 plasma no absorption is observed, hence ruling out the possible contribution of oxygen negative ions or other argon and oxygen species.

In conclusion, F^- negative ions have been detected by direct observation of the weak continuum absorption below 364.5 nm due to photodetachment, using the cavity ring-down technique. The F^- densities in $Ar/CF_4/O_2$ and $Ar/C_4F_8/O_2$ plasmas were in the range of (0.5–3) $\times10^{11}$ cm^{-3}. The densities were not significantly different for single (27 MHz) or dual (2+27 MHz) frequency excitation, not confirming recent PIC simulation predictions, although experiments with higher 2 MHz power must be performed to clarify this point. A continuum background absorption was also observed, which was strongest with C_4F_8 at high flow rates, but was suppressed by O_2 addition. The origin of this continuum has not been confirmed but may be due to CF_3^- negative ions, larger carbon-containing molecules, or dust particles which are destroyed by the addition of oxygen. Preliminary measurements of the electron density by a hairpin resonant probe have indicated that the negative ion to electron density ratio is ~ 2 in $Ar/CF_4/O_2$ and ~ 10 in $Ar/C_4F_8/O_2$ dual frequency discharges. These results will be presented in more detail in a future publication.

The authors wish to thank Lam Research Corporation for donation of equipment and financial support.

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