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Laser diagnostics for bulk and near-surface detection of atomic hydrogen and oxygen in plasma environments

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The Ohio State University, 1994
LASER DIAGNOSTICS FOR BULK AND NEAR-SURFACE DETECTION
OF ATOMIC HYDROGEN AND OXYGEN IN PLASMA
ENVIRONMENTS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

By
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A. Significance of rf discharges

The importance of glow discharges has been realized through the widespread use of low-energy plasmas in the electronics industry for the fabrication of microscopic circuit components, the deposition of materials, the modification of surface structures, and to the production of novel devices. Numerous examples include the plasma etching of Si and SiO$_2$ in CF$_4$ discharges,$^1$ the surface passivation of compound (GaAs) surfaces in H-containing discharges,$^{2-4}$ the chemical vapor deposition of diamond films in various hydrocarbon discharge mixtures,$^{5,6}$ and the production of GaAs FET with a hydrogenated channel.$^7$ Plasmas are used because they generate chemically reactive radicals from relatively inert molecular gases through electron impact dissociation, i.e. they achieve high-temperature chemistry without the use of high temperatures. In addition, they provide a means for achieving selective surface chemistry (obviously required for microdevice structures), through the directional transport of ions and electrons across the sheaths to masked device surfaces.
Despite the successful use of plasmas in producing desired device structures, their application has been mostly empirical in nature over the years. Scientists and application engineers have realized that an empirical understanding of the complex chemistry and physics of plasma environments is not sufficient to support the expanding spectrum of their applications. Therefore, an increasing demand for better understanding the underlying mechanisms that govern the plasma-surface interactions has been recognized, as only few processes have been optimized for the range of desired results. An effort to elucidate some of the fundamental physics and chemistry of plasma environments has been undertaken by the scientific community, that will allow better control and optimization on already existing procedures, as well as the development of alternative or even new processes of device fabrication.

From the broad variety of discharges of great technological interest, we have chosen to study hydrogenic and oxygenic discharges. H$_2$ plasmas have immediate application in the processing of III-V materials. H$_2$ and H$_2$/CH$_4$ plasmas are used to directly etch GaAs and InP$^8,9$ and also to passivate surface defects of GaAs$^3$. Therefore, it is our objective to study H$_2$ plasmas and investigate the influence of III-V materials, under loaded reactor conditions, on the measured characteristic quantities of the discharge. On the fundamental side, a hydrogen plasma is relatively simple, so one has reasonable hope for
fundamental understanding of the H₂ rf plasma, that is necessary for the complete understanding of more complex plasma systems. For example, much of our work could be applied to model H₂/CH₄ plasmas used to diamond thin film growth.¹⁰ Oxygenic plasmas also have wide applications in the processing of microelectronic devices, for the anisotropic etching of SiO₂ and the stripping of photoresists.

A description of a plasma environment, a partially ionized gas nearly characterized by charge neutrality, would require measurement of the particle densities (ions, electrons, neutrals), of the distribution functions, as well as of the electric fields which drive charged particle transport. All these quantities are coupled by the Boltzmann equations¹¹ which relate the rate of production and loss of particles by collisions to the flow of particle flux by means of the flux gradient and the force fields. Especially, measurements of quantities that determine the plasma-surface interactions are important, because they address a problem of obvious technological interest and of inherent scientific complexity. Hence, it is our intention to discuss the detection of those major gas-phase reactive species that influence surfaces exposed to the discharge.

B. Reactive plasma species and their interaction with surfaces

Atomic species and radicals can be readily produced in discharges via
electron-impact dissociation of parent molecules and have significant concentrations. Most atoms or radicals of processing interest have considerable chemical reactivity in their ground state, a property of great importance in surface interactions. As their volume recombination lifetimes are long, these reactive species can diffuse across the entire discharge volume and reach the reactor surfaces where they may chemically combine with solid materials. Independently from the details of the way that the reaction proceeds, it results in gradients of the reactive species concentration adjacent to surfaces. The prominence of the concentration gradients is indicative of the degree of reactivity between the species and the surface. Therefore, measurements of the concentration of radicals especially close to surfaces are very important in determining whether the presence of this species can cause modification of the surface characteristics towards a desired direction. For example, the etching of Si in a CF₄ discharge that is caused by the formation of a volatile compound (SiF₄) is indicated by the appearance of a significant concentration gradient for CF₂ and CF₃ radicals. The reactivity of a species on a surface is also indicated by the species decay kinetics; a rapidly decaying population of a species in a discharge (at a rate higher than its volume recombination) suggests species removal at the surface as a result of chemical reactivity. It is important, however, that measurements of the reactivity of radicals with surfaces are made
in-situ, since one cannot exclude the influence of charged species on the measured surface characteristics.

The extent to which gas-surface chemical reactions can be enhanced by energetic radiation (ions and electrons) incident on the surface has been the subject of extended studies on plasma etching that revealed evidence for ion- and electron-assisted chemical reactions. There are many ways in which the charged species may cause enhancement of the reactivity of radicals with surfaces: (1) Dissociative chemisorption may occur preferentially at defect sites produced by ion or electron bombardment. (2) Electron and/or ion bombardment may cause an adsorbed molecule to dissociate, a situation that would normally happen. (3) Removal of the adsorbed layer by ion and/or electron bombardment so that etching proceeds beyond a monolayer of adsorbed gas. (4) Bond breaking may allow penetration of adsorbed atoms (beneath the surface) which then react with the substrate. (5) Enhancement of residue removal by bombardment (in case of formation of involatile reaction products) that is necessary for the reaction to proceed.

Although etching is only one example of surface-plasma interactions, one may expect that mechanisms similar to the ones described above may affect the surface reactivity of radicals in similar ways. Therefore, the issue of reactivity of atoms with surfaces should be correctly addressed by performing the
measurements in the presence of charged species that bombard the surfaces exposed to the discharge. The results of \textit{in-situ} measurements should then be compared to previous measurements of the surface reactivity, typically performed downstream of a discharge,\textsuperscript{16} and possible disagreement between them would be used as an indication for ion-enhanced chemistry.

Throughout this work, concentrations of atomic species (the most abundant reactive species in partially ionized plasmas) produced in a parallel plate reactor will be measured in H\textsubscript{2} and O\textsubscript{2} rf discharges. It is important that these measurements be performed with high spatial and temporal resolution, as it is obvious from the above discussion. This requirement has led us to the choice of an appropriate diagnostic tool that will be discussed in the next section.

C. Diagnostic technique

The ideal characteristics of a plasma diagnostic include the capability of \textit{in-situ} measurements so that we do not infer information about the plasma from downstream measurements or extracted samples, in which case we are led to possible loss of information about the spatial and temporal behavior of the identified species and in some cases to ambiguities in species identification. We also desire \textit{non-intrusive} diagnostics so that our measurements do not perturb
the system under investigation and alter the parameters that characterize it. High spatial and temporal resolution are also desired in an ideal diagnostic, since it is in the spatial and temporal behavior of the species that the signature of the pathways responsible for the production and loss of these species lies. Obviously, the degree of desired resolution depends on and varies with the discharge parameters, but generally speaking the spatial resolution should be better than the size of the plasma sheath\textsuperscript{17,18} to allow investigation of the discharge structure, and the temporal resolution should be much smaller than the period of the discharge to permit non-time-averaged measurements.

It becomes obvious from the previous discussion that laser-based techniques comply with all the requirements for an ideal diagnostic. Laser beams can penetrate through optical windows to discharge environments without perturbing them. By strongly focusing the laser probe, it is possible to restrict the interaction with the discharge to a small volume which can be translated throughout the discharge and thus provide information with a high spatial resolution, basically determined by the laser beam size. The temporal resolution is limited to the laser pulse width which is typically less than 10 ns, therefore, with the addition of timing electronics (to the detection system) that synchronize the firing of the laser with a particular phase of a discharge, we can extract information about possible modulation of parameters characterizing the
discharge within one rf cycle. These advantages are fully employed throughout our efforts to provide important information about H₂ and O₂ discharges. An overview of laser-based and other diagnostic techniques, such as mass-spectrometry, the complimentary nature of which should be definitely recognized, is given in References 19 and 20.

The detection of reactive plasma species (atoms, radicals, ions, and metastables) became possible only recently by laser-induced fluorescence (LIF) that makes use of tunable lasers in conjunction with non-linear light generation techniques realized by the use of non-linear crystals. LIF schemes are available and have been realized in the detection of many radicals of particular relevance to reactive plasma processing, such as CF and CF₂, BCl, CCl, of ions such as N₂⁺ and Cl₂⁺ and of metastables such as F⁺ and Ar⁺. The detection of atoms in their ground level such as H(1s²S) and O(2p⁴ 3P) is more demanding and feasible only by means of two-photon allowed laser-induced fluorescence (TALIF), since these species have excited levels lying to energies accessible only by VUV radiation, difficult to produce and transmit through most media. Both, one-photon and two-photon LIF techniques provide excellent quantum-state selectivity and reduce the noise of the measurements by easily discriminating the signal against the bright plasma-induced emission background that is typical of plasma environments. Also, the requirement of high photon
flux necessary at the probe region to compensate the extremely small crosssections for TALIF transitions results to high spatial resolution, as laser beams must be focused as tightly as possible without the undesirable effect of powersaturation of the transition. Although technologically more demanding, TALIF schemes have been used to the detection of several atomic species such as N, Cl, O, and H in various discharges.

The next question one needs to answer is what kind of information about the discharges could be retrieved from the employment of these diagnostics. First and most importantly, the species concentrations are necessary to the understanding of discharge chemistry since measurements of these can provide tests for kinetic models. Concentrations can be easily measured by LIF or TALIF since (in the absence of depopulating mechanisms) the signal is proportional to the ground state concentration, and can be further put on an absolute scale by directly comparing the signal to that corresponding to a known species concentration. This is an important advantage of the LIF techniques with respect to other optical diagnostics such as emission spectroscopy, in which case many excitation mechanisms could be responsible for the observed signal. In addition, if these concentrations are measured as a function of the position in the discharge and as a function of time after initial discharge turn-on and/or turn-off, information about the kinetics of these species can be inferred, and in
some cases formation and loss processes responsible for these species can be
discriminated from a variety of mechanisms present in the complex plasma
environments.

Careful analysis of the line shapes and Doppler-broadened linewidth
measurements can lead to in-situ measurements of energy distributions, due to
the species relative motion along the direction of beam propagation. Neutral
species in their ground state in a discharge have shown thermal\textsuperscript{37,38} or almost
thermal\textsuperscript{39} translational energy distributions, while atomic photofragments of
laser-dissociated molecules carry the excess of chemical binding energy, thus
providing a means for parent molecule identification\textsuperscript{40,39} Measured rotational
energy distributions appear to be thermal due to rapid rotational-translational
energy transfer, while vibrational distributions are likely to be non-thermal
making it possible that vibrationally hot molecules play an important role in
plasma chemistry. Measurements of ion translational distributions especially in
the sheaths are of great importance to plasma etching studies as well as to
studies of charge-exchange mechanisms.

Finally, Stark effect perturbations observed in LIF data have allowed
local electric fields to be measured in a discharge\textsuperscript{26,41} This is due to the fact
that, in the presence of an electric field, energy levels are shifted or new lines
(not expected by the selection rules) appear as a function of the electric field.
The method has shown field strengths in the range of a few V/cm to a few KV/cm.

In conclusion, laser-based diagnostics and specifically LIF techniques are well-suited for measurements as basic as concentration profiles as well as for other plasma characteristics such as energy distributions and electric fields. In this thesis spatially and temporally resolved concentration measurements will be presented as a useful means for determining the species reactivity with bounding surfaces, and will hopefully provide input to and a test for numerous existing computational plasma models.

The material for this thesis is organized as follows: First, we introduce the reader to the essence of laser-based diagnostics and specifically to the TALIF technique we employed to measure concentrations of H and O atoms in rf discharges. Chapter II will describe the details of the experimental techniques that led to absolute concentration measurements. Investigation of possible mechanisms depopulating the laser-excited level and thus leading to erroneous results is also presented in this chapter. In Chapter III, we present experimental results for spatial and temporal profiles for H atoms in the rf discharge under both unloaded and loaded reactor conditions. Detailed analysis of the concentration gradients close to bounding surfaces and of the decay rates in the discharge afterglow is also presented and leads to determination of the loss
coefficients for H atoms on a variety of surfaces of interest in the microelectronics industry. In a similar fashion to Chapter III, Chapter IV describes spatially and temporally resolved O-atom concentration measurements, and our understanding of the O-atom kinetics in terms of loss mechanisms both in the discharge and in the afterglow. Finally, Chapter V briefly summarizes our results pointing out the significance of these in-situ measurements to provide information about the surface characteristics and their alteration by the discharge.
Plasma diagnostic studies have become more useful with the wide spread implementation of laser induced fluorescence (LIF) to directly probe transient species in radio frequency plasma reactors.\textsuperscript{42} LIF and, particularly, multiphoton techniques have been proved valuable tools for sensitive detection of atoms, radicals and ions because of their unique advantages that include high spatial and temporal resolution. Quantitative results, preferably \textit{absolute} concentrations, can be compared to computational models to obtain a better understanding of plasma processes. They can also be used as input to optimize dry processing conditions. Time-resolved concentrations can give direct information on formation and decay rates of species of interest in the plasma and can be used to determine the mechanisms for the creation of different reaction products.

In this chapter we will describe the experimental set-up that allowed the employment of two-photon absorption laser-induced fluorescence (TALIF) diagnostics for the measurement of absolute concentrations of ground state atomic hydrogen and oxygen, spatially and temporally resolved, in a parallel
plate rf plasma reactor. The calibration for the determination of absolute atomic concentrations was accomplished in our system by the employment of a titration technique based on known atom concentrations in a discharge flow reactor. Similar techniques have successfully been applied in combustion related experiments as well as in filament-assisted diamond growth experiments. Fluorescence signals obtained in the discharge flow reactor were correlated to ones measured under identical excitation and detection conditions in the parallel plate reactor system. We thereby obtained absolute concentrations of atomic hydrogen and oxygen in plasma environments under conditions typically found in plasma assisted material processing: pressure in the range 0.1-3 Torr, frequency 10 MHz, and rf power in the range 10-100 W (power density: 0.28-2.8 W/cm³).

A. Experimental set-up

The radio-frequency (rf) reactor was a six-way pyrex vessel with water-cooled stainless-steel electrodes of equal area (50 mm in diameter), fitted onto the vertical ports at an adjustable separation; typically the interelectrode gap was set to 19 mm. A schematic of the parallel plate reactor with the electrodes in horizontal configuration is shown in Fig. 1. The top electrode was driven by a power supply operating at 10 MHz while the bottom electrode was grounded.
Figure 1. Schematic of a parallel plate rf reactor translating in X-Z directions with respect to excitation/detection region.
The reactor cell, mounted on a X-Z translation stage which was motor driven and controlled by a personal computer, was translated with respect to the fixed excitation/detection arrangement. As a result, we were able to monitor discharge regions across the interelectrode space (axial profiles) as well as parallel to the electrode surface (radial profiles) with a minimum step of 3 μm. The actual spatial resolution however was limited by the laser spot size, estimated to be 100 μm in diameter. Therefore, a spatial step of 100 μm was typically chosen to probe atomic concentrations at near-surface discharge regions.

The pressure of H₂ and O₂ gases was usually maintained at 3 Torr and the flow rate was adjusted and measured by a Tylan flow controller. The discharge operated at 10 MHz was driven by a Hewlett Packard 3325A Synthesizer-Function generator, then amplified by an ENI Model 3200L RF power amplifier with a Heathkit SA-2060A Antenna Tuner. The discharge power was routinely maintained at 10 W with the current and voltage waveforms monitored and measured on a Tektronix Model DSA 601 digital oscilloscope.

The repetitive pulsed mode of the discharge was accomplished by amplitude modulation of the output of the signal generator by means of a homemade adjustable gate. Typical rf pulse widths were 2-3 ms at a repetition
rate of 20 Hz. The switching times were measured by monitoring the voltage pulse applied at the powered electrode and the current pulse flowing through a resistor in series to the discharge. Both the rise and the decay times were found to be 3-4 μs. The plasma induced emission was also followed and it was found to rise in about 20 μs and to decay in 2-3 μs. The delay between the onset of the discharge and the laser firing could be adjusted by means of a computer controlled delay generator.

The experimental lay-out is shown in Fig. 2 together with the excitation scheme for hydrogen atoms. The laser system consisted of a Quanta-Ray DCR-2A Nd-YAG laser operating at 20 Hz that was used to pump a Quanta-Ray PDL-2 dye laser operating on SR-640 dye for H-atom detection. The dye laser output, centered around 614 nm for this experiment, was frequency doubled by a Quanta-Ray WEX operating with a KDP crystal. After matching the polarization of the 614 nm and 307 nm beams, we combined both beams in a CSK β-Barium Borate (BBO) "A" crystal. A 205 nm beam with a pulse energy of 0.5 mJ was routinely obtained and it was focused at a spot in the interelectrode gap, by a 150 mm focal length lens. Two 205 nm photons provided the 97492 cm⁻¹ energy necessary to induce a transition from the 1s²S ground state to the 3d²D and 3s²S states.

The Balmer alpha emission from the excited state, detected perpendicular
Figure 2. Schematic of experiment set-up and excitation scheme for H-atom detection.
to both the laser and the electrode axis, was collected by a system of focusing lenses. Directed through a 10 nm FWHM interference filter centered at 656 nm, the fluorescence was detected by an ITT Model 4123 gated photomultiplier tube (PMT), or by a much faster Hammamatsu R928 continuous tube in cases where measurement of the fluorescence decay was desired (as in the measurements of quenching rate coefficients that will be presented in section C) and where the anode current was much less than the tube specifications. The PMT signal was fed directly to a Tektronix DSA601 digital scope where it was integrated and averaged. In order to decrease the random fluctuation of the TALIF intensities due to the laser power fluctuation, we occasionally normalized the signal to the laser power; the laser power was monitored by a Molectron power meter. Both the photodiode and the PMT signals were fed into the digitizer and processed appropriately to account for the quadratic dependence of a two-photon excitation scheme. Finally, the normalized signal was transferred to a personal computer.

Similarly to 205 nm light necessary to induce the TALIF transition in hydrogen, 226 nm light, in resonance with the two-photon transition from the ground \(2p^4 \, ^3P\) state to the \(3p^3P\) state in oxygen, was produced by mixing the fundamental of the Nd/YAG laser at 1064 nm with the second harmonic of the output of the dye laser (operating on a mixture of R590 and R610 dyes dissolved in methanol) at 572 nm. The experimental lay-out and the oxygen
Figure 3. Schematic of experiment set-up and excitation scheme for O-atom detection.
TALIF scheme are shown in Fig. 3. The 226 nm probe beam was directed into
the cell parallel to the electrode surface, and it was focused to a spot inside the
plasma reactor by means of a 150 mm quartz lens. The upper state fluoresces
to the $3s^3S$ by emission at 844.6 nm that was detected at right angles with
respect to the excitation beam by a PMT through a 845 nm interference filter.

B. Absolute concentration calibration technique

The discharge flow reactor designed for the calibration of the hydrogen
TALIF signals is shown in Fig. 4. The experiment was designed to allow
replacement of the top electrode of the parallel plate rf reactor by a microwave
discharge reactor while all other components were maintained unchanged.
Therefore, excitation/detection geometry and efficiency were identical in both
cases and signals produced by the microwave discharge could be directly
compared with those in the rf discharge. Hydrogen atoms were produced in a
microwave discharge as a $H_2$/Ar mixture (5% $H_2$) was flowing in a quartz tube
through a Microtron 200 air cooled Evenson cavity. The flow rates of $H_2$ and
Ar were measured with MKS and Tylan flowmeters respectively. The mixture,
flowing downstream from the microwave discharge region, was introduced into
the outer portion of a coaxial glass tube entering the reactor cell. The inner tube
that carried the titrant gas, NO$_2$, had perforations at its end allowing the gases
Figure 4. Schematic of the flow-tube reactor used for absolute calibration of TALIF signals.
to mix well and react before entering the laser probe region. It was wrapped on its outer surface with teflon tape to reduce losses of H atoms as they were flowing towards the mixing region. NO$_2$ was supplied by an equilibrium mixture of N$_2$O$_4$/NO$_2$ maintained in an ice bath to prevent condensation of NO$_2$ at the input of the Tylan flowmeter. To calibrate small H-atom concentrations in the detection region, a dilute mixture of NO$_2$ in Ar (10% NO$_2$) was used, to achieve small flow rates for the titrant gas, below the controllable range of the flow controllers.

Hydrogen atoms generated in the microwave discharge, as described above, were introduced into the probe region and detected with the TALIF technique. As NO$_2$ molecules were slowly introduced into the mixing region, they reacted with H atoms according to the fast titration reaction

$$H + NO_2 \rightarrow OH + NO \quad (1)$$

Secondary reactions such as OH + OH $\rightarrow$ H$_2$O + O and O + OH $\rightarrow$ O$_2$ + H which would change the [NO$_2$]/[H] stoichiometry from 1:1 to 1.5:1, are significantly reduced at the low [H] measured here. Other interfering reactions such as OH + H$_2$ $\rightarrow$ H$_2$O + H can also be made negligible by diluting the H$_2$ in an inert gas such as He or Ar. The H atom TALIF signal linearly decreases with increasing NO$_2$ concentration (inset of Fig. 5) until it becomes indistinguishable from the background (end-point of titration). The concentration
**Figure 5.** Calibration curve for H-TALIF signals. Each data point is determined by a titration curve, as shown in inset.
of NO₂ which is necessary to remove all H atoms (x-intercept in inset of Fig. 5) equals the concentration of H atoms at the beginning of the titration, given the 1:1 stoichiometric ratio of the reaction. We verified that the mixing of the reactant gases was complete by adjusting the position of the mixing region within the outer tube, until the end point of the titration was sharply determined. The probe region was a few millimeters downstream from the end of the coaxial flow tube in order to keep the background fluorescence from the glass tube as low as possible, while at the same time we maintained a H-atom density as close as possible to that at the mixing region, before the flowing gas diffused over the larger rf reactor volume. We have conducted measurements of the variation of the H-atom concentration with the distance from the end of the tube and made small corrections to the calibrated intensities accordingly.

Fig. 5 shows the calibration curve which was constructed for different H atom concentrations in the flow reactor. The TALIF intensities shown were taken with a 205 nm pulse power of 0.5 mJ. All signals taken at different laser powers must be referenced to this power, given the quadratic dependence of the TALIF signals on the 205 nm photon intensity. A minimum observable concentration has been established at < 10¹³ atoms/cm³ which is determined by the instability of the microwave discharge at such low hydrogen concentrations. However, the plasma induced emission from the 10 MHz rf discharge is a
greater source of noise than the microwave instability and, therefore, we have not pushed this lower concentration limit further.

The in-situ titration technique used for H atoms can be also used to estimate the concentrations of O atoms that were produced by flowing a dilute mixture of O$_2$/Ar through the Evenson microwave cavity. Their concentration at the detection region was probed by TALIF, as O atoms were mixed with NO$_2$ and reacted according to:

$$O + NO_2 \rightarrow NO + O_2$$

(2)

By measuring the NO$_2$ concentration at the end-point of the titration (see inset of Fig. 6), we were able to estimate the concentration of O atoms corresponding to the TALIF intensity before the introduction of NO$_2$ in the flow tube. In Fig. 6, we show the calibration curve we constructed by repeating the titration experiment at constant laser power for various O-atom concentrations produced in the flow tube. The calibration curve shows a linear dependence of the TALIF signal on O-atom concentrations, indicating that TALIF is a valid diagnostic for O atoms across the concentration range we examined. Data points taken at higher concentrations than the ones shown on the graph fall below the calibration line, indicating depopulation of the 3$^3$P level by a mechanism (possibly stimulated emission).
Figure 6. Calibration curve for O-TALIF signals. Each data point is determined by a titration curve, as shown in inset.
C. Effect of quenching on concentration measurements

Since we were interested in measuring H and O-atom concentrations over a wide range of pressures, it was necessary to investigate the effect of quenching of the laser-excited state by surrounding molecules, as pressure increases. Obviously, if relaxation of laser-excited atoms to lower levels occurs through non-radiative channels due to collisions with gases such as H\textsubscript{2} and O\textsubscript{2}, it may result in significantly reduced LIF signals that need to be corrected appropriately. The quantum yield Q of the TALIF transition, defined as the time-integrated fluorescence signal normalized to the initial one (Q=I/I\textsubscript{0}), was measured as a function of pressure, in an experiment where a constant H and O-atom density was produced by photolysis of C\textsubscript{2}H\textsubscript{2} and NO\textsubscript{2} respectively by the photolysis/probe laser at constant power. The pressure of the precursor gases (C\textsubscript{2}H\textsubscript{2}, NO\textsubscript{2}) was maintained at ~100 mTorr in a non-flowing cell, while the pressure of the quenching gases (H\textsubscript{2}, O\textsubscript{2}) was increased from a few hundreds mTorr to as high as an atmosphere. The TALIF signal was collected by a relatively fast PMT (with a rise and fall time 2 and 5 ns respectively), and the output waveform was both, time-averaged on the digitizer to yield I/I\textsubscript{0} values, and stored in the computer. Afterwards, the effective radiative lifetime \( \tau \) of the laser-excited atoms was determined by fitting a single exponential decay function to the data. Since all the measurements that will be presented in this
Figure 7. Quenching of laser-excited H(n=3) atoms by H₂, measured by means of lifetimes \((\tau/\tau_0)\) and time-integrated signals \((I/I_0)\).
Figure 8. Quenching of laser-excited O$(3^3P)$ atoms by O$_2$, measured by means of lifetimes ($\tau/\tau_0$) and time-integrated signals ($I/I_0$).
work were taken at pressures no greater than a few Torr, we will show results for quenching over this low-pressure range.

The decrease of the quantum yield $Q$ of the fluorescence due to the quenching of $\text{H}(3d, 3s)$ and $\text{O}(3^P)$ as a function of pressure of $\text{H}_2$ and $\text{O}_2$ is indicated by representative data shown in Table 1. The results from both methods (time-integrated fluorescence signals and lifetimes) are shown on $1/Q$ versus $P$ plots (in Figs. 7 and 8), from where the total deexcitation rate coefficients $k$ were determined. Generally speaking, the range of pressure over which measurements of the quantum yield of the fluorescence were possible is broader via time-integrated area measurements than via effective radiative lifetime ones, as the latter are limited by the temporal response of the PMT. However, results from both methods are in good agreement (over the common pressure range), as indicated by the values of the total deexcitation rate coefficients noted on Figs. 7 and 8 (determined by the shown linear fits). A kinetic model was developed\textsuperscript{18} to describe the quenching data for $\text{H}$ atoms. In this model, the mechanisms of non-radiative deexcitation and $1$-state mixing were included, as to be accounted for the total deexcitation of the $\text{H}(n=3)$ atoms through channels different than those resulting to 656-nm emission. Independently from the nature of the mechanisms that lead to the deexcitation of laser-excited atoms, the measurements of the quantum yield of the
TABLE 1. Representative data for quenching of H\((n=3)\) and O\((3^3P)\) atoms by H\(_2\) and O\(_2\), respectively.

<table>
<thead>
<tr>
<th>Quenching</th>
<th>P (Torr)</th>
<th>Q ((\tau/\tau_0))</th>
<th>Q ((I/I_0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>of H((n=3)) by H(_2)</td>
<td>0.05</td>
<td>0.94</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.91</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.78</td>
<td>0.78</td>
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<tr>
<td></td>
<td>0.30</td>
<td>0.70</td>
<td>0.73</td>
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<td></td>
<td>0.55</td>
<td>0.60</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>-</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>1.10</td>
<td>-</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>1.85</td>
<td>-</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>2.85</td>
<td>-</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>3.85</td>
<td>-</td>
<td>0.22</td>
</tr>
<tr>
<td>of O((3^3p)) by O(_2)</td>
<td>0.04</td>
<td>0.97</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>0.82</td>
<td>0.68</td>
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<tr>
<td></td>
<td>0.18</td>
<td>0.80</td>
<td>0.62</td>
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<td></td>
<td>0.32</td>
<td>0.75</td>
<td>0.49</td>
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<tr>
<td></td>
<td>0.62</td>
<td>0.39</td>
<td>0.40</td>
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<tr>
<td></td>
<td>0.92</td>
<td>0.31</td>
<td>0.28</td>
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<td></td>
<td>1.54</td>
<td>0.24</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>1.92</td>
<td>0.23</td>
<td>0.19</td>
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<tr>
<td></td>
<td>2.42</td>
<td>0.19</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>2.93</td>
<td>-</td>
<td>0.17</td>
</tr>
</tbody>
</table>
fluorescence can be used empirically to correct TALIF signals measured at pressures above a few hundred mTorr, depending on the environment where H or O atoms are detected.

D. Effect of amplified stimulated emission (SE)

When determination of the absolute concentrations of species in the excited state is desired, an understanding of all the physical mechanisms that may depopulate the laser-excited state is necessary. Furthermore, a correction has to be made to the quantum yield of the fluorescence for every detectable depopulation mechanism.

In atomic oxygen, the two-photon-excited $2^3\text{P} \rightarrow 3^3\text{P}$ transition is followed by fluorescence to the $3^3\text{S}$ level. The rapid population of the $3^3\text{P}$ level in conjunction with the short lifetime (1.8 ns) of the lower $3^3\text{S}$ level$^{49}$ can create population inversion between these two levels. Consequently, SE is not uncommon in this classic three-level system and it may compete with laser induced fluorescence or with multiphoton ionization$^{50}$ in the depletion of the excited state. Studies of the effect of SE on the quantum yield of the fluorescence seem complicated by the fact that conditions in reactive environments (flames, combustion, discharges), under which SE can be detected, vary significantly. A kinetic model was recently developed to simulate
the effect of ASE on the population of the laser-excited state O(3P), however the actual number densities were unknown.\textsuperscript{51} Two-photon-excited stimulated emission in the H system has been also detected in flames,\textsuperscript{52-54} where the 656-nm Balmer-\(\alpha\) radiation was readily observable by eye propagating in both the forward and reverse directions.

To search for SE in our experiments, a glass slide and neutral density filters were placed on the back optical window of the rf cell from where the laser beam exits after it interacted with atoms in the discharge. Thus, the main portion of the laser beam was blocked by the glass and filters, so that only 656-nm or 845-nm SE radiation was collected through appropriate interference filters by the R928 PMT sitting in the forward direction of the laser beam. Although SE in atomic oxygen was easily observed in the rf reactor, SE in atomic hydrogen was not observed. Therefore, we will describe our observation of SE in the oxygen discharge only. A method to determine a threshold for SE in terms of absolute concentration of O atoms was developed, by observing SE simultaneously with absolutely calibrated LIF signals. We found that this threshold constitutes a rather constant concentration of O atoms (even at varying excitation laser power) above which the level of SE increases abruptly. Further, we will discuss the conditions under which the influence of the SE on the fluorescence should not be neglected.
Figure 9. Titration curves for LIF and SE signals corresponding to the same initial O-atom concentration, taken at different laser powers. (flow: 100% = 7.3 sccm)
Our method of determining a threshold for SE requires simultaneous observation of LIF and SE signals with a calibration procedure for the LIF signal. In Fig. 9, we present data from three titration experiments done under identical conditions with the exception of the laser power that was decreased significantly from 185 to 44 μJ/pulse (Fig. 9 (a) to (c)). For each experiment, LIF and SE signals were measured as the flow of NO₂ was increased up to the end-point of the titration, noted by the x-intercept of the linear fit to the LIF data. Since the conditions in the flow tube were identical for all three experiments presented in Fig. 9, the end-points occur at the same titrant gas concentration that correspond to the same initial O-atom concentration (5.2x10¹⁴ atoms/cm³). Notice that the SE signals increase rapidly as the NO₂ flow decreases (or equivalently the O-atom concentration increases) beyond a cross-over region in titrant gas concentration. We define this cross-over between the linear dependence of the SE signal on the O-atom concentration and the asymptotic approach to zero as the threshold for SE. The existence of such threshold is expected by the very nature of SE. The plots in Fig. 9 indicate that, despite the difference in laser power, the threshold for SE occurs at not significantly different O-atom concentrations (2.1, 2.5, and 2.9x10¹⁴ atoms/cm³, in (a), (b), and (c), respectively). This is probably due to the fact that, we may be close to the saturation point of the transition, therefore even a significant
increase in laser power (as in Fig. 9 (a)) does not necessarily lead to a significantly higher LIF signal and thus significantly lower threshold for SE. To check whether data are taken under saturation conditions, we measure LIF signals as a function of laser power, as shown in Fig. 10. A straight line with a slope of 2 is expected in the logarithmic plot of the LIF signal as a function of the laser power, since \( I \propto P_{\text{laser}}^2 \) for a two-photon process. We observe a deviation from the straight line at 60 \( \mu \text{J/pulse} \) indicating where the transition has reached saturation. Therefore, the LIF signal in Fig. 9 (b) and (c) increases quadratically with laser power, while it deviates from its quadratic dependence as the laser power continues to increase (Fig. 9(a)).

We repeated the titration experiments at various conditions through changes in the O-atom concentration, at constant excitation laser power. In Fig. 11, we show two titration curves taken at the same low laser power (44 \( \mu \text{J/pulse} \)) and different O-atom concentrations (6.6 and 5.2 \( \times 10^{14} \) atoms/cm\textsuperscript{3}, Fig. 11(a) and (b), respectively). Effort was made to keep the partial pressures of Ar and O\textsubscript{2} almost unchanged in the cell and as low as possible, so that the quenching of the upper excited state remains the same and does not affect significantly the LIF (and thus the SE) signals. Similar to our result in Fig. 9, we find that SE takes place above a rather constant threshold value of O-atom concentration (2.9 \( \times 10^{14} \) atoms/cm\textsuperscript{3}). We also observe that, although the LIF
Figure 10. O-TALIF signal (I) as a function of the laser power (P). The solid line that fits the low-power data (P < 60 μJ/pulse) has a slope of 2, as expected for a 2-photon process.
Figure 11. Titration curves for LIF and SE signals corresponding to different initial concentrations. The threshold for SE occurs at similar O-atom concentrations. (flow: 100% = 7.3 sccm)
signal is rather linear in O-atom concentration (Fig. 11(b)), the LIF signal in Fig. 11(a) exhibits saturation-like characteristics at low NO$_2$ flow or equivalently at high O-atom concentrations. This is probably due to significant depopulation of the excited state by the mechanism of SE at high O-atom concentrations, that affects the LIF signal, as we will discuss in detail below. In general, from a total of 11 experiments in which a threshold for SE was observed and in which the O-atom concentration was varied from 4.1 to 7.4x10$^{14}$ atoms/cm$^3$ and the laser power from 0.04 to 0.51 mJ/pulse, we conclude that the threshold for SE occurs at a concentration of (2.46±0.4)x10$^{14}$ atoms/cm$^3$. The theoretically determined threshold in the work of Huang and Gordon was estimated to be two orders of magnitude smaller, for an effective path length of the active medium z=1cm. However, if a smaller value of z is used (more appropriate for our experimental conditions, as the focal point is estimated to be 100 $\mu$m) a higher concentration of ground state atoms is needed to provide a significant gain in the system that will induce SE (G=exp(ΔNσ$_e$z), where G is the gain, ΔN is the population inversion density (proportional to the ground state concentration), σ$_e$ is the cross section for SE and z is the effective path length of the active medium). Therefore, the experimentally determined threshold for SE in this work is in semiquantitative agreement with the model proposed by Huang and Gordon.
Figure 12. Titration curve for a LIF signal strongly deviated from linearity due to significant SE. This deviation (~40%) is the highest observed in our experiments. (flow: 100% = 88 sccm)
Efficient depopulation of the $3^3P$ level by the SE channel will cause a deviation from linear response of the LIF signal as function of O atom concentration. We seek such deviation in our data as an indication for the influence of SE on LIF. Fig. 12 shows the strongest influence of SE on the LIF signal that has been observed in our measurements. The LIF signal is linear up to a certain O-atom concentration above which exhibits saturation-like behavior. However, the effect is not larger than 50%. We expect this reduction of the LIF signal due to SE to be a complicated function of many variables; the laser power, the O-atom concentration, and environmental conditions (pressure, type of gas, etc.). For example, as pressure or the percentage of oxygen increases (oxygen is a better quencher than Ar)\(^7\), the quenching of the $3^3P$ level is getting more efficient, therefore the LIF signal decreases and SE is getting less efficient and subsequently it affects less the LIF signal.

The general method presented here, for evaluation of a threshold for SE and investigation of the SE influence on LIF, can be applied to a large variety of systems. A plasma reactor, for instance, is one of the most important systems that people use today for a wide variety of applications. Therefore, we chose to demonstrate the method in a rf cell. The titration system has been detached from the rest of the reactor and a planar water-cooled stainless steel electrode has been mounted in its place, opposite to an identical electrode. The ground
Figure 13. Pressure dependence of LIF and SE signals in a rf reactor. The (corrected for quenching) LIF signals deviate from linearity with pressure after the appearance of SE.
state O(2^3P) atoms were generated in the RF reactor operating at 10 MHz. Pure oxygen has been used at pressures in the range 0-2 Torr. The data for LIF and SE signals as functions of pressure are presented in Fig. 13. The LIF signal has been corrected for the increase in quenching of the upper state by O₂, as the pressure of oxygen rises (the quenching rate constant was measured in the rf reactor in a separate experiment\textsuperscript{59}). Absolute concentrations are also given in Fig. 13. The SE signal rises abruptly from zero at about 0.3 Torr where the concentration of ground state O atoms, as shown by the LIF curve in the figure, is about 3x10\textsuperscript{14} atoms/cm\textsuperscript{3}. One can immediately see that the deviation from linearity of the corrected LIF response with pressure starts after the appearance of SE. The observed deviation may be a result of two mechanisms. One possible candidate is sublinear production of O atoms in the plasma reactor due to a decrease in the efficiency of the discharge with increasing pressure or an increase in O-atom recombination as pressure increases. A second candidate is the effect of the SE on LIF, but certainly a combination of the two can not be excluded. Thus, 50\% is an upper limit to the effect of SE on the LIF signal in a 1.5 Torr discharge.

We believe that the method we presented here is a general diagnostic tool that can be easily applied to many other systems with similar spectroscopic characteristics. Certainly, it can be applied in complicated environments (such
as flames, combustion, discharges, etc.) to distinguish the effect of the stimulated emission against other competing mechanisms that perturb the population of the laser-excited state. Although we did not observe a significant effect of the SE on the fluorescence in the environments that we investigated, we can not exclude appearance of a strong effect in other systems.
CHAPTER III
H-ATOM CONCENTRATION MEASUREMENTS

Since radio frequency (rf) plasmas are employed extensively in microelectronic processing, a more complete understanding of the complex plasma environments is of considerable importance. In-situ and non intrusive measurements of particle densities, temperatures and electric fields can provide insight into complex mechanisms governing plasma and device surface interactions. The spatial distribution of ground state atoms, the most abundant reactive constituents of a plasma, is especially important in near-surface regions since existence of concentration gradients would indicate reactivity of the atoms with the surface. Furthermore, since the kinetics of atomic species are indicative of creation or destruction mechanisms in the discharge, the temporal evolution of the atomic species should be probed. In the next two chapters, we will show spatial profiles for atomic hydrogen and oxygen concentrations measured across the interelectrode gap of a rf discharge at steady state. By means of a pulsed discharge (a technique employed in the past in studies of BCl₃, CF₄, CF₄/O₂ and H₂/Ar discharges) the evolution of the spatial profiles can be followed.
during both the built-up and the decay of the atomic population, after initial turn-on and turn-off of the discharge, respectively. We therefore utilize spatially and temporally resolved TALIF measurements to provide information on the production and loss of atoms in chemical plasmas. This work will be extended to measurements of the reactivity of atomic hydrogen and oxygen with various surfaces of significant interest in the microelectronics industry, e.g. Si, GaAs, photoresists, etc., as it will be discussed at the last sections of chapters III and IV.

A. H-atom profiles

A typical axial profile of H-atom concentration at different positions across the interelectrode space of a continuous RF discharge and above the center of the electrode is shown in Fig. 14. It was taken with the laser frequency sitting at the peak of the transition, while the translation stage was stepped to different positions across the 19 mm gap. All the spatial profiles shown in this work are corrected for the occultation of the detection solid angle from the electrode surface as the distance between the laser beam and the electrode surface gets smaller than 3.5 mm. A calculation of the reduction of the solid angle from which we collect the 656 nm fluorescence was experimentally checked. We filled the reactor cell with C$_2$H$_2$ at a pressure of 50
Figure 14. Typical H-atom concentration profile as a function of the distance from the ground electrode (at 0 mm) in a 10 MHz continuous H₂ discharge.
mTorr and we detected H atoms produced by photolysis of the acetylene molecule with 205 nm photons.\textsuperscript{39} Since the detection of H atoms takes place immediately after their production, within a laser pulse duration (10 ns), the concentration is independent of the position of production anywhere in the interelectrode space. The reduction in the TALIF signal that we observed was a result of the viewing reduction of the solid angle as the laser beam approached the electrode surface, which is determined by the detection/collection geometry. We have found that the experimental determination of the geometrical view factor agrees within 10\% with that calculated by geometrical considerations.\textsuperscript{20} As shown in Fig. 14, a concentration of about $3 \times 10^{14}$ atoms/cm\textsuperscript{3} stays relatively constant over a wide region around the center of the discharge. As we approach the electrode surfaces, however, the concentration drops sharply to zero within 3-4 mm away from each electrode surface. We will discuss the mechanism that resulted in the observed concentration characteristics in the next section, where we will model the observed spatial and temporal behavior of the concentrations. The solid line in Fig. 14 results from the proposed model (see section B) and shows a reasonably good agreement with the measurements.

Spatial profiles of hydrogen atoms were also taken in a pulsed discharge at different times after the discharge was turned on. In Fig. 15, we show the spatial distribution of H atoms at 0.25 ms, 1 ms, and 2.5 ms. The figure
Figure 15. Temporal evolution of H-atom spatial profiles after the onset of a pulsed discharge; experimental data and simulated results at $t=0.25$, 1.0, and 2.5 ms.
describes the temporal evolution of H atoms; The profile at 0.25 ms clearly shows that H atoms are generated at regions centered at about 3.4 mm away from each electrode surface. The 1.0 and 2.5 ms traces show how the steady state distribution builds up. H atoms exit the production regions and fill the interelectrode space until they approach the metallic electrode surfaces, where they stick or recombine. The profile at 2.5 ms closely resembles that shown in Fig. 14, taken in a continuous RF discharge, indicating that a steady state is essentially established in the discharge at this point in time.

The profiles in Fig. 16 represent typical H-atom distributions after the discharge is turned off at t_0. The spatial profiles shown are taken at elapsed time t after t_0, with t=0.25 ms, t=0.5 ms, and t=1 ms. It is clear that the electrodes represent a significant sink for H atoms in the system. The solid lines shown in Figs. 15,16 represent best fitted theoretical concentration profiles which we will discuss later in this chapter (section B).

Fig. 17 shows a temporal profile of the hydrogen atom concentration at the center of the discharge. The discharge was turned off at t_0=2 ms, a time close to the establishment of an equilibrium concentration in the discharge. The decay of hydrogen atoms follows a single exponential law at t-t_0>0.3 ms (t_0=2 ms), as indicated by the linearity of the logarithmic fit displayed also in Fig. 17, that is independent from the atomic concentration at the time the discharge was
Figure 16. Decay of H-atom spatial profiles in the afterglow of a discharge (turned off at $t_0=2$ ms); data and simulated results at 0.25, 0.5, and 1.0 ms after $t_0$. 

Distance from bottom electrode (mm)

H-atom concentration ($10^{15}$ cm$^{-3}$)

- $t=0.25$ ms
- $t=0.5$ ms
- $t=1.0$ ms

fit
Figure 17. Temporal profile of H-atom concentration in a pulsed discharge (turned off at $t_0=2$ ms). A single exponential fits well the H-atom decay in the afterglow ($t>2$ ms).
turned off. The exponential decay reveals that first order kinetics are responsible for the decay of hydrogen atom concentration after the discharge was turned off, with a time constant \( \tau = 1.03 \pm 0.08 \) ms. Therefore, gas phase recombination of the hydrogen atoms is not significant since it would result in second order kinetics with respect to H atom concentration.

Finally, we replaced hydrogen by deuterium to check for any quantitative differences in behavior due to their mass difference. From the decay of the atomic deuterium concentration we determined a time constant \( \tau = 1.66 \pm 0.10 \) ms. The comparison of the time constants of hydrogen and deuterium indicated an approximate \( m^{1/2} \) dependence on the mass of the decaying particles. The experimental observations presented above will guide us in the formulation of a model to be presented next.

B. Model

The observation of the first-order decay for H atoms in the afterglow, as well as the existence of significant concentration gradients adjacent to electrode surfaces suggest that surface removal is the dominant process for H atom destruction in the 3 Torr H\(_2\) discharge. Also the \( m^{1/2} \) dependence of the decay rates suggests that diffusion is the dominant mechanism governing the evolution of the atomic concentrations in the discharge we study. Therefore, a simple
model for the mass transport by diffusion from the production regions towards
the boundaries, where heterogeneous processes for the H atom removal exist,
may describe the spatial and temporal measurements presented above. The
model incorporates the following assumptions: First, the gas phase
recombination is negligible as indicated by the simple exponential decay of the
atomic hydrogen population. Second, the H atoms are destroyed only on the
metallic electrode surfaces which induce catalytic recombination and therefore
represent sinks for H atoms. Third, neutral diffusion governs the movement of
the H atoms towards regions of reduced atomic concentration in both the
discharge and the afterglow. Finally, the production of H atoms takes place in
narrow regions in the discharge. These regions roughly coincide with the visibly
brightest portion of the plasma, indicative of regions of high excitation and
dissociation. The production of energetic species at regions located several
millimeters away from the surfaces, has been indicated previously for species
such as F* metastables, O atoms, and BCl radicals at high frequencies.

Since our detection point is usually centered above the electrode surfaces,
the diameter of which (50 mm) is a lot bigger than the distance between them
(19 mm), a one-dimensional model would be sufficient for the description of
our data in the rf cell. The general case of two boundary surfaces with loss
coefficients \( \gamma_1 \) and \( \gamma_2 \) is considered, so the model provides a way to quantify the
gas-surface interactions. Let the production of H atoms take place at point sources near the sheaths (as the experimental evidence presented in section A supports) localized at distances \( x=x_0 \) and \( x=a-x_0 \) from the electrode surfaces separated by a distance \( a \). Although the production of H atoms takes place over the time scale of the period of the discharge (100 ns), we are mostly interested in a time-averaged production over a millisecond time-scale, given the fact that the temporal behavior shown in Fig. 17 exhibits a characteristic time of \( \sim 1 \) ms.

A time-averaged production \((\text{at a constant rate } R_0)\) can be represented by two equally-weighted delta functions, \( R_0[\delta(x-x_0) + \delta(x-a+x_0)] \), centered at the sources \( (\text{i.e. at } x_0, a-x_0) \). The surface removal of H atoms gives rise to gradients in the concentration \( \rho \) which depend on the reactivity between the atomic species and the surface and can be expressed in terms of a loss coefficients \( \gamma \), defined as the ratio of the flux of particles lost to the total flux of particles impinging on a surface. The flux of particles lost on a surface located at \( x=0 \) is \( J=D(\partial \rho/\partial x)_{x=0} \) (according to Fick's law), while the flux of particles that impinge on the surface and recoil is \((v\rho/4)_{x=0}\),\(^{17}\) where \( D \) is the diffusion coefficient, \( v \) is the mean thermal velocity of H atoms, and \( \rho_{x=0} \) is the gas-phase atomic concentration at the surface. A definition of \( \gamma \),

\[
\gamma = \{D(\partial \rho/\partial x)/[D(\partial \rho/\partial x) + (v\rho/4)]\}_{x=0}
\]

(3) exhibits reasonable behavior in the limits \( \rho=0 \) and \( \partial \rho/\partial x=0 \), corresponding to
totally absorbing ($\gamma=1$) and totally reflecting surfaces ($\gamma=0$) respectively. 

Equation (3), written for two surfaces located at $x=0$ and $x=a$ with loss-coefficients $\gamma_1$ and $\gamma_2$ respectively, can be rearranged to give the following expressions for the boundary conditions of our problem:

\[
\frac{\partial \rho}{\partial x}|_{x=0} = \left[\nu \rho \gamma_1 / [4D(1-\gamma_1)]\right]_{x=0} \quad (4a)
\]

\[
\frac{\partial \rho}{\partial x}|_{x=a} = \left[-\nu \rho \gamma_2 / [4D(1-\gamma_2)]\right]_{x=a} \quad (4b)
\]

Thus, the one-dimensional diffusion equation that includes production of H atoms at a rate $R_0$ is

\[
\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} + R_0[\delta(x-x_0) + \delta(x-a+x_0)] \quad (5)
\]

The general solution of Eq. (5), subject to the boundary conditions given in Eqs. (4a) and (4b), can be expressed as a series (see Appendix A),

\[
\rho(x,t) = \sum \rho_n(x)[1-\exp(-D\lambda_n^2t)] \quad n=1,2,3,...
\]

where

\[
\rho_n(x) = (2R_0/aD\lambda_n^2)\cos(\lambda_n x-\delta_n)[\cos(\lambda_n x_0-\delta_n)+\cos(\lambda_n(a-x_0)-\delta_n)],
\]

(7)
\( \lambda_n \) is the \( n \) root of the equation,

\[
\lambda_n \alpha = \tan^{-1}\left[\gamma_1 v/(4(1-\gamma_1)D\lambda_n)\right] + \tan^{-1}\left[\gamma_2 v/(4(1-\gamma_2)D\lambda_n)\right] + n\pi,
\]

(8)

and the phase \( \delta_n \) is given by

\[
\delta_n = \tan^{-1}\left[\gamma_1 v/(4(1-\gamma_1)D\lambda_n)\right]
\]

(9)

For simplicity, we tried first to fit Eqs. (6) and (7) to the experimentally determined spatial profiles shown in Figs. 14, 15, and 16 with \( \gamma = 1 \) (totally absorbing surfaces). These equations fit well the steady-state \((t \to \infty)\) spatial distribution (Fig. 14), as well as the spatial profiles at various times after turning the discharge on (Fig. 15) or off (Fig. 16), as it is demonstrated by the best fit curves (obtained by a least square fit program) shown with solid lines in these figures. Thus, we estimated the position of the sources to be at 3.4 \( \pm \) 0.2 mm away from the electrode surfaces, the production rate \( R_0 \) to be \((16 \pm 2) \times 10^{16} \) atoms/cm\(^2\)sec and \(31 \times 10^{16} \) atoms/cm\(^2\)sec in the pulsed and the cw discharge respectively (operated at 5 W and 10 W), and the value of the diffusion coefficient \( D \) to be 380 \( \pm \) 60 cm\(^2\)/s. This value agrees well (within the uncertainty) with that of 440 cm\(^2\)/s as calculated from Gilliland's semiempirical equation.\(^{62}\) This equation based on kinetic theory assumes a \( T^{3/2} \) dependence for the diffusion coefficient and it is evaluated at 300 K (we assume thermally equilibrated H atoms at room temperature).
Figure 18. The steady-state concentration gradients for H and D atoms at small distances from the SS electrode surface determine a loss coefficient $\gamma_{ss}=5\%$. 
However, the experimental concentration gradient near the electrode surfaces (Fig. 14) is smaller than that calculated from Eqs. (6) and (7), an indication that the electrode surfaces are partially absorbing with a loss coefficient $\gamma_{ss}$ for H atoms. A better fit was obtained by solving the diffusion equation for boundary surfaces with a loss coefficient $\gamma_{ss} = 5 \pm 1\%$ for hydrogen and deuterium atoms, as shown in Fig. 18. The loss coefficients for hydrogen and deuterium are equal, as one would expect from Eq. (3) since the mean thermal velocity and the diffusion coefficient both vary as $m^{1/2}$. This result further verifies the fact that the balance between diffusion and atom removal at the surface establishes the observed concentration gradient close to the electrode surfaces.

In the afterglow of the discharge (turned off at $t=t_0$), the solution of Eq. (5) becomes:

$$\rho(x,t) = \sum \rho_n(x) [1 - \exp(-D\lambda_n^2 t_0)] \exp[-D\lambda_n^2 (t-t_0)] \quad n=1,2,3,\ldots(10)$$

As it is obvious from the linearity of the semilogarithmic plots (Fig. 17) for times $t-t_0 > 0.3$ ms, only the first term of Eq. 10 is significant and this fact dictates a predominant decay of the H population with a rate $k_d = -D\lambda_1^2$, where $\lambda_1$ is the first root of Eq. (8). Higher order terms in Eq. 10 are important only for times $t-t_0 \leq 0.2$ ms, while they contribute less than 5% in the decaying
concentration at times $\geq 0.2$ ms after the discharge is turned off. The first term of the series relates the time constant $\tau$ of the exponentially decaying H concentration to the diffusion coefficient $D$: $1/\tau = D\lambda_1^2$. We thus calculate the diffusion coefficients for H and D atoms to be $355 \pm 30 $ cm$^2$/s and $220 \pm 15$ cm$^2$/s respectively. Actually, the comparison of the diffusion coefficients of these atoms provides a test for the model discussed above, since the diffusion coefficient depends inversely on the square root of the mass of the diffusing particle. The estimated values essentially agree with the expected $2^{1/2}$ ratio within the experimental uncertainty.

In Fig. 19 we have plotted the variation of the steady-state concentration of H atoms (normalized to its value at $x=3$ mm) over a small distance from the electrode surface that bears the surfaces of various $\gamma$'s in a 3 Torr H$_2$ discharge, as calculated from Eq. (6) with $t \to \infty$. As one expects, surfaces with small $\gamma$ result in almost flat concentration profiles, while surfaces with larger $\gamma$'s result in significant concentration gradients adjacent to them. From the figure, we also observe that although the concentration gradients do not change significantly for $\gamma$ in the range 0.1%-1%, they do vary sharply at higher values of $\gamma$: 1%-50%.

In Figs. 20 (a) and (b) we have plotted the calculated decay rates as a function of the loss coefficient of H atoms on the boundary surfaces. The expected decay rates vary monotonically as a function of the loss coefficient of
Figure 19. Simulations of the variation of H-atom concentration over a small distance from a surface characterized by a loss coefficient $\gamma$ varied from 0.1% to 100%.
Figure 20. Simulations of H-atom concentration decay rates in the discharge afterglow as a function of the loss coefficient $\gamma$ of the electrode surface.
a surface. At the pressure of 3 Torr, used throughout the experiments presented above, Fig. 20 (a) shows that the decay rates increase by a factor of 5 with $\gamma$ varying from 0.1%-1%, and by a factor of 2 only in the next range $1\% \leq \gamma \leq 10\%$, while the decay rates almost plateau at higher values of $\gamma > 10\%$. Furthermore, Fig. 20 (b) indicates that the sensitivity range for $\gamma$ is extended to well above 10% at a much smaller pressure (0.3 Torr).

To conclude, decay rates obtained from the temporal profiles can accurately determine small loss coefficients, since $k_d$ is proportional to $\gamma$ in the limit where $\gamma \rightarrow 0$. For example, the sensitivity to determine $\gamma$ for H atoms in a 3 Torr discharge is reasonable for $\gamma < 10\%$, while for higher $\gamma$ values a typical experimental error ($\pm 10\%$) would result in a significant error in determining $\gamma$ ($\geq \pm 40\%$). However, spatial profiles provide more accurate means to yield and extend the upper limit of accurately determined $\gamma$ values to $\sim 50\%$. Otherwise, temporal profiles should be taken in a smaller discharge pressure (for example in 0.3 Torr) that allows extension of the range of accurate $\gamma$ values (to $\sim 50\%$, as shown in Fig. 20 (b)).

C. Loaded $H_2$ discharges

Since the first report of Si etching by neutral hydrogen atoms in a low pressure plasma,$^{63}$ radio frequency (rf) reactors have been widely employed in
the fabrication of microscopic devices. The application of reactive plasma methods in silicon technology has been extended to the technology of GaAs as well, for deposition, etching, cleaning and passivation. Beyond the wide use of these discharges, there is however a need for a more fundamental understanding of plasma-surface interactions. In particular, space and time resolved optical measurements are used to monitor the distribution and development of reactive species, and therefore help to elucidate the mechanisms that lead to processing of device surfaces. In this section, we will describe spatial and temporal profiles taken in H₂ discharges loaded with surfaces of technological interest in microelectronics industry; Si and GaAs semiconducting surfaces and metallic surfaces. Quantitative analysis of the spatial and temporal distribution of H atoms leads to an estimation of the reactivity between the species and the surface, in terms of the fraction of the flux of species that are removed by the surface, as we discussed in section B.

The samples that we loaded in the rf reactor were n-type GaAs and Si (100, 111) substrates, used without being treated, of 0.5 mm thickness. We simply placed them centered on the ground bottom electrode, very much like loading industrial processing reactors. Different metal films (~ 0.2 μm) were deposited on Si wafers in a micro-etch ion-milling vacuum system. The typical diameter of the substrates loaded in our reactor was 50 mm, when axial profiles
(along the interelectrode space) were taken, so that the electrode surface was completely covered. This way we eliminated any effects caused by the non-homogeneity of electrode surfaces on the axial profiles of H atoms. However, the substrate diameter was reduced to 10 mm for the radial profiles (parallel to the electrode surface) to be taken, as it will be described in the following paragraph.

To demonstrate the dependence of the spatial distribution of H atoms on the nature of the substrate surface, we measured spatial concentrations 1.5 mm above the grounded bottom electrode (bearing the substrate) while the reactor cell was translated horizontally (radial profiles). The radial profile shown in Fig. 21(b) was taken over a 10x10 mm GaAs wafer. We observe a significant increase in hydrogen atom concentration localized over the wafer surface. A radial profile over an identical stainless steel piece, shown in Fig. 21(a), proved that the drastic change in the concentration could not be attributed to changes in the bulk properties of the discharge, or in the detection geometry, but rather to the nature of the GaAs surface. We further verified that, by depositing 2-μm-thick gold on the GaAs wafer. A radial profile taken over the gold-coated GaAs wafer, shown in Fig. 21(c), indicates a reduction in the hydrogen concentration and suggests that certainly a surface/atomic hydrogen interaction must be responsible for the variation in the measured atomic concentrations.
Figure 21. Comparison of H-atom radial profiles probed 1 mm above a (a) stainless-steel, (b) GaAs, and (c) gold-coated (10x10 mm) substrate, placed on the ground electrode.
Figure 22. Evolution of H-atom spatial profiles after the onset of a pulsed discharge loaded with a GaAs wafer on the ground electrode; data points at t=0.15, 0.5, and 2.5 ms.
By employing a *pulsed* discharge, we studied the temporal development of the hydrogen concentrations in the interelectrode space. In Fig. 22 we show hydrogen atom concentrations in a discharge loaded with a 15 cm² GaAs wafer at various times after the onset of the discharge. Specifically, the spatial concentrations shown were measured at times $t=0.15$ ms, $0.50$ ms and $2.50$ ms. The profile at $t=0.15$ ms indicates that the production of hydrogen atoms in these plasmas occurs in localized regions in close proximity to the electrodes. In time, the hydrogen atoms diffuse from their sources towards the center and the electrode surfaces. We observe that the spatial profile at very early times is not affected by the presence of the GaAs wafer, however, as time increases, the concentration of the hydrogen atoms builds up close to the wafer surface, resulting to the apparent spatial asymmetry of the profile taken at time $t=2.5$ ms.

Spatial variations in the steady-state concentration of H atoms in a 10 W, 3 Torr $\text{H}_2$ plasma are shown in Fig. 23. Data points were taken every 0.5 mm along the interelectrode distance, and the intensities were converted to absolute concentrations by means of a titration technique described in Chapter II. The concentrations have been also corrected for the quenching of the laser-excited state by $\text{H}_2$ at 3 Torr. It appears that the presence of various materials that cover the bottom electrode (with a stainless-steel top electrode) alters the spatial
Figure 23. Spatial profiles of H-atom concentration at steady-state discharge conditions with the indicated materials (Al, Si, Ni) loaded on the ground electrode (at 0 mm). Shown are fits from Eqs. (6), (7).
distribution of atomic hydrogen in the interelectrode space, and results in concentration gradients varying from nearly zero adjacent to Si and Al surfaces to much higher values near stainless-steel (SS) and Ni surfaces.

The temporal behavior of the H concentration in the afterglow of the plasma for 40 W input power in 3 Torr H\textsubscript{2} is shown in Fig. 24, with the measurements taken at 2 mm from the bottom electrode surface of the indicated material. The H concentration decays much faster near the Ni and SS surfaces than near the Al or Si surfaces. The decays are single exponential, as shown by the linearity of the semi-logarithmic plots, for all the materials present on the electrode surface with the exception of data points taken at very short time (t-t\textsubscript{0} < 0.3 ms) in the case of SS and Ni.

The simple diffusion model described in section B was used to fit the experimental data of the spatial profiles at equilibrium (t→∞), the determined parameters being the production rates R\textsubscript{0} and the loss coefficients, γ\textsubscript{i}, of the surfaces. The solid lines shown in Fig. 23 are the results of such fits with the values of γ\textsubscript{i} given in the first column of Table 2. These γ\textsubscript{i} values were compared with the results of measurements of the recombination coefficient of H atoms on surfaces in previous experiments\textsuperscript{16,69} (see Table 2, column 3). The result for Ni is in good agreement with that from the flow tube experiments, but γ\textsubscript{Al} and γ\textsubscript{Si} are much smaller. We believe that a thin layer of oxide, known to
be formed easily on these surfaces, is responsible for the discrepancy. In fact, oxidized surfaces are typically characterized by recombination coefficients in the order of 0.1%.\textsuperscript{16}

From least square fits of the experimental decays shown in Fig. 24, the loss coefficients for Al, Si, SS and Ni were estimated, and are given in the second column of Table 2. These fits required to fix the loss coefficient for the opposite electrode (SS), which was estimated from the spatial profiles ($\gamma_{ss}=3.0\pm 1.4\%$). Both spatial and temporal profiles lead to similar values for the loss coefficients, as shown in Table 2.

**TABLE 2. H atom surface loss coefficients**

<table>
<thead>
<tr>
<th></th>
<th>This work</th>
<th>Previous investigations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>spatial</td>
<td>temporal</td>
</tr>
<tr>
<td>Al</td>
<td>0.18±0.03 %\textsuperscript{a}</td>
<td>0.20±0.01 %\textsuperscript{a}</td>
</tr>
<tr>
<td>Si</td>
<td>0.30±0.03 %\textsuperscript{a}</td>
<td>0.25±0.02 %\textsuperscript{a}</td>
</tr>
<tr>
<td>SS</td>
<td>3.0±1.4 %</td>
<td>4.5±0.2 %</td>
</tr>
<tr>
<td>Ni</td>
<td>18±3 %</td>
<td>20±9 %</td>
</tr>
</tbody>
</table>

\textsuperscript{a} oxidized materials

\textsuperscript{b} See Ref. 16.

\textsuperscript{c} See Ref. 60.

\textsuperscript{d} See Ref. 69.
Figure 24. Temporal profiles of H atoms taken in the discharge afterglow ($t>2$ ms) and fits with parameters the loss coefficient $\gamma$ of the surfaces.
The uncertainties shown in the table represent the confidence in determining \( \gamma \) by fitting a single profile (as in Figs. 23 and 24) to Eqs. 3 and 6. The error of \( \gamma_{SS} \), in particular, is determined from four spatial profiles taken over a period of a month. Typically, the day-to-day reproducibility of the data leads to a variation of \( \gamma \) up to 50%.

D. Modification of the surface loss coefficient by the plasma

a. Permanent modification

Because of the great importance of H\(_2\) plasmas in semiconductor processing, we exposed Si surfaces (of 111 and 100 type) in low-pressure (0.5 Torr) H\(_2\)/Ar plasmas, operated in the continuous mode. After every exposure of the surface to the low-pressure plasma for a few minutes, we measured the temporal decay of H atoms over the treated Si surface in the afterglow of a 3 Torr H\(_2\) plasma. Fig. 25a shows a few representative temporal decays taken after exposure times \( T = 0, 1.5, 3, \) and 16.5 minutes, respectively. The variation of the decay rates with \( T \) is shown in Fig. 25b. We observe that the decay rate increases drastically initially, while it plateaus after an exposure time \( T \approx 5 \text{ min} \).

This observation could result from removal of the oxide from the Si surface that has been previously reported to enhance the H consumption due to etching of SiO\(_2\) and subsequent etching of Si.\(^{60}\) However, analysis of the Si
Figure 25. (a) Temporal decay of H atoms near a Si surface exposed to a low pressure H\textsubscript{2}/Ar discharge for T=0, 1.5, 3.0, 16.5 min. (b) Decay rates of H atoms as a function of exposure time T.
surfaces after their treatment in the plasma, by means of \textit{ex situ} x-ray photoelectron spectroscopy (XPS), showed an unexpected change in the surface composition; a small amount of iron was deposited on the surface (estimated to be \( \sim 5\% \) after a 10 min exposure in the low-pressure H\(_2\)/Ar plasma), possibly the result of sputtering that is favored at low pressures. The measurement of the decay rates in the 3 Torr pulsed discharge could not alter the characteristics of the treated surface due to the low duty cycle of the pulsed discharge and the inefficiency of ion bombardment on the surface at the pressure of 3 Torr. An estimation of the loss coefficient that corresponds to the maximum value of the decay rate shown in Fig. 25b \((\gamma=3.5\%\)) is consistent with deposition of iron on the Si surface. We conclude that sputtering can cause alteration of the loss coefficient of a surface (and thus of the spatial and temporal profiles) in a direction characterized by the deposited material. The loss coefficient increases if the deposited material is characterized by a loss coefficient higher than that of the surface (as in the case of SS deposited on SiO\(_2\)), and it decreases in the opposite case. Obviously, any reduction of the SiO\(_2\) from the surface would be screened by the deposition of iron, since both effects would tend to increase the recombination coefficient of the surface.

Similar observations were made at a GEC rf Reference Cell installed at Wright Laboratories,\(^7\) where sputtering of electrode material onto substrates
caused significant discrepancies between spatial profiles taken a few days apart, after long exposure of the substrate surfaces to the discharge. These observations reveal unintentional sputtering of electrode material in loaded discharges and demonstrate the sensitivity of the LIF diagnostics to detect, in situ and in real-time, changes induced by energetic plasmas on exposed surfaces.

These observations of unintentional sputtering in our reactor as well as in the Reference Cell at Wright Laboratories indicate that sputtering may be present in many industrial systems (since they are similar to our reactors) and it could lead to undesirable or deleterious effects on surfaces treated in processing reactors. And although it would be difficult to eliminate it, unintentional sputtering could be certainly reduced, once researchers are aware of its occurrence.

In order to investigate the etching of SiO$_2$ from the Si substrate surfaces in low-pressure H$_2$ discharges, we replaced the SS electrodes with Al ones, so that we prevent an increase of $\gamma$ due to iron sputtering. Since Al surfaces are characterized by similar decay rates as Si ones, one would expect to readily observe the native oxide removal after long exposure to a low-pressure and high-power H$_2$ discharge. However, we did not observe any change in the decay rates of the H atoms, within the experimental error, even after a 20 minute
exposure of the surface in the discharge. This indicates that surface oxides of Si continue to cover the semiconducting surface during the time we performed the experiment. Possibly, in situ generation of H$_2$O due to reaction of H atoms with the surface oxides (SiO$_2$) or with the pyrex walls of the reactor favors the reformation of these oxides on the surfaces, as water does not readily desorb from the passivated surfaces at room temperature.$^{4,71}$

b. Temporary modification

From temporal profiles for H atoms taken in a pure H$_2$ discharge confined by Al electrodes, we observed a temporary change of the surface loss coefficient as a function of pressure. This observation is important since processing plasmas are routinely operated at pressures 1-10 mTorr, much lower than that we have used so far (3 Torr). We operated the discharge in the pulsed mode (low duty cycle). The pressure was varied from 4 Torr down to 0.2 Torr and the temporal decay of the atomic hydrogen was measured at 2 mm above the bottom-electrode surface. In Fig. 26 we show the variation of the decay rates as a function of pressure. The solid lines represent the calculated variation of the decay rate $k_d$ with pressure for various $\gamma$'s (according to $k_d=-D\lambda_1^{-2}$, where $\lambda_1$ is the first root of Eq. (8)), assuming that H atoms are at room temperature. As shown in Fig. 26, it appears that the loss coefficient of Al increases 2-3 times as pressure decreases from 4 to 0.2 Torr. We believe that
Figure 26. Variation of the decay rate (and the loss coefficient) of H atoms over an Al surface as a function of the discharge pressure.
surface damage or enhanced gas-surface chemistry due to ion bombardment (ion-neutral synergism)\textsuperscript{15} could be responsible for this observation. A possible increase of the species temperature with pressure\textsuperscript{39} would enhance this effect even more, since it would lead to an estimation of an even smaller loss coefficient for H atoms at elevated temperatures (at high pressures), as $k_i$ is in a first approximation proportional to $\gamma v \sim \gamma T^{1/2}$. The observed change is only temporary since the alteration of the loss coefficient of the surface with pressure is consistently reversible, \textit{i.e.} the variation of $\gamma$ with pressure is independent from the history of the surface in the discharge, unlike the modification of the Si surface due to sputtering described in part a of section D.

In conclusion, the nature of a surface exposed to a discharge affects the concentration gradients and the decay rates of atomic hydrogen close to the surface in a way characteristic of the material. This fact allows the loss coefficients for H atoms on these surfaces to be determined. Finally, the removal rate of reactive atoms by a surface was found to depend on mechanisms such as sputtering and ion bombardment, that often alter the surface characteristics in energetic plasma environments.
CHAPTER IV
O-ATOM CONCENTRATION MEASUREMENTS

The important role that O atoms play to the stripping of polymers\textsuperscript{72} and the anisotropic etching of SiO\textsubscript{2} in CF\textsubscript{4}/O\textsubscript{2} plasmas\textsuperscript{73,74} has dictated the extensive use of optical diagnostics in recent years, for direct or indirect detection of their ground state population. Optical emission spectroscopy\textsuperscript{75} has been used to monitor relative variations of atomic oxygen concentrations in etching plasmas, while the need for quantitative measurements of the ground state concentrations has led to the use of actinometric optical emission (AOE). Since actinometry is not reliable as a means to monitor ground state concentrations under certain discharge conditions,\textsuperscript{76} time-resolved actinometry\textsuperscript{77} and two-photon laser-induced fluorescence\textsuperscript{36,61,78} were then used to investigate the parameter space of applicability of AOE spectroscopy. Optical diagnostics employed in pulsed discharges allow study of the kinetics of O atoms,\textsuperscript{79} an understanding of which would allow optimization of, and a better control over, microelectronics fabrication conditions.

In this chapter, we will describe two-photon absorption laser-induced
fluorescence as a diagnostic to determine absolute O-atom concentrations, their spatial distribution indicative of the production regions, and their temporal profiles that are found to be sensitive functions of the discharge parameters.

A. Oxygen atom profiles

O-atom concentrations were measured under steady state conditions in the rf reactor as a function of the discharge pressure and power. The TALIF signals have been corrected for the quenching of the laser-excited state at elevated pressures (as we discussed in chapter II). In Fig. 27, we show absolute concentrations in a 20 W discharge for the pressure range 0-4 Torr. The deviation of the concentration from linearity occurs at pressures higher than 1 Torr, and it is probably due to gas-phase removal of O atoms (enhanced at high pressures) or due to depopulation of the laser-excited level by SE (as we discussed in chapter II). However, even at the highest pressure measured (4 Torr), the deviation from linearity is less than 30%. The degree of dissociation of the oxygen discharge is also shown in Fig. 27, and it is estimated to \(~2\%\), slightly decreasing as pressure increases. The power dependence of the O-atom concentration in a 3 Torr discharge is shown in Fig. 28. The concentration increases rapidly initially, slowly at powers around 50 W, and finally decreases at powers higher than 80 W. The degree of dissociation, estimated again to be
Figure 27. Absolute O-atom concentrations and % dissociation as a function of the discharge pressure (pure O₂).
Figure 28. Absolute O-atom concentrations and % dissociation as a function of power in a pure O₂ discharge.
~ 2 %, exhibits a similar behavior. The reduction in dissociation at high powers is indicative of the presence of a loss mechanism for O atoms that is enhanced at high powers.

Spatial profiles obtained in a 3 Torr O\textsubscript{2} discharge are shown in Fig. 29. Both traces obtained in a pulsed discharge, at time t=0.25 ms and t=1.8 ms respectively after initial turn-on, exhibit the same qualitative characteristics; they are mostly uniform throughout the interelectrode space with small concentration gradients near the electrode (stainless-steel) surfaces. The uniformity of the profile taken very early in the discharge (t=0.25 ms) indicates a rather uniform production of O atoms in the interelectrode space (in contrast to H-atom production which was found occurring predominantly near the plasma sheaths, as we discussed in Chapter III), while the small concentration gradients close to electrode surfaces indicate relatively small losses for O atoms on the electrode surfaces.

A typical temporal profile, obtained by means of a pulsed discharge at 3 Torr, is shown in Fig. 30 (a). Semilogarithmic plots of the O-concentration versus time after discharge turn-off exhibit linear behavior, characteristic of a first order mechanism responsible for the decay of the atomic oxygen. As in the case of hydrogen atoms evolving in a discharge (described in Chapter III), heterogeneous reactions of O atoms with the surface material can explain the
Figure 29. Spatial profiles of O-atom concentration at $t=0.25$ and 1.8 ms after discharge turn-on indicate a small loss coefficient ($\gamma = 0.5 \pm 0.1 \%$) for a SS surface.
observed single-exponential decay. We can exclude gas-phase reactions between O atoms and other molecules (present in an oxygen discharge), such as

\[ O + O_2 + O_2 \rightarrow O_3 + O_2 \]  
\[ O + O_3 \rightarrow 2O_2 \]

that could lead to single-exponential decays (if the concentrations of \( O_2 \) or \( O_3 \) were considered as constant during the decay of O) since they result in decay rates (calculated from the rate constants of the corresponding reactions) much smaller than those we measured experimentally.

B. Model

The above presented observations have led us to the formulation of a diffusion model, similar to that presented in the previous chapter, to describe the spatial and temporal O-atom profiles. Oxygen atoms are produced at a rate \( R_0(\chi) \) nearly homogeneously throughout the interelectrode space, and they are removed by heterogeneous processes on the surfaces. The surface loss of O atoms is expressed by the loss coefficients \( \gamma_1, \gamma_2 \) of the two electrode surfaces, and it is embodied in the boundary conditions. Therefore, we solve the following diffusion equation for the mass transfer of O atoms in the interelectrode space:
\[
\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} + R_0(x) \tag{13}
\]

We tried a variety of functions to express the production term for O atoms: two-point sources symmetrically located at the sheaths of the discharge (as in the hydrogen discharge) or a uniform production throughout the interelectrode space. The appropriate function for \( R_0(x) \) was chosen for producing the best fit to the spatial profile (Fig. 29) taken at \( t = 0.25 \text{ ms} \), since the spatial profiles at longer times or at steady-state are not sensitive to the form of \( R_0(x) \). The best results were obtained for a uniform production of O atoms throughout a region extended from a distance \( x_0 \) from either electrode surface. It is convenient for the analytical solution of Eq. (13) to assume that the production rate \( R_0(x) \) results from a continuous distribution of planar sources located at distances \( x' \) from the electrode surface at \( x = 0 \), with \( x' \) ranging from \( x_0 \) to \( a-x_0 \) (i.e. the production region). We can then conveniently express such a production term as an integral

\[
R_0(x) = R_0 \int \delta(x-x')dx' , \tag{14}
\]

over the interelectrode space \([x_0, a-x_0]\).

The solution of Eq. (14) has the general form

\[
\rho(x,t) = \sum \rho_n(x)\{1-\exp(-D\lambda_n^2t)\} , \tag{15}
\]
where
\[
\rho_n(x,t) = \left[2R_0/(aD\lambda_n^3)\right]\cos(\lambda_n x - \delta_n)[-\sin(\lambda_n x_0 - \delta_n) + \sin(\lambda_n (a - x_0) - \delta_n)],
\]
(16)

\(D\) is the diffusion coefficient, \(v\) is the mean thermal velocity of O atoms, and \(\lambda_n, \delta_n\) are given by the following equations, respectively.

\[
\lambda_n a = \tan^{-1}\left[\gamma_1 v/(4(1-\gamma_1)D\lambda_n)\right] + \tan^{-1}\left[\gamma_2 v/(4(1-\gamma_2)D\lambda_n)\right] + n\pi,
\]
(17)

\[
\delta_n = \tan^{-1}\left[\gamma_1 v/(4(1-\gamma_1)D\lambda_n)\right]
\]
(18)

Eqs. (15)-(18) are used to fit the experimental data with parameters \(x_0, \gamma_1, \gamma_2,\) and \(R_0\). The value used for the diffusion coefficient for O was 80 \(\text{cm}^2/\text{s}\) at 3 Torr and at room temperature. The fit curve on the spatial distribution at \(t=0.25\,\text{ms}\) (Fig. 29) was obtained for O atoms uniformly produced in the interelectrode region extended from \(x_0=1.2\,\text{mm}\) from each electrode surface and destroyed on surfaces (SS) with a loss coefficient \(\gamma=(0.5 \pm 0.1)\,\%\). For the rest of the fit curves that will be shown in this work, \(x_0\) is used as a (determined) constant.

The solution of Eq. (13) with the production term \(R_0(x)\) equal to zero, in the afterglow of a discharge \((t>t_0)\), is given by

\[
\rho(x,t) = \sum \rho_n(x)\{1-\exp(-D\lambda_n^2t_0)\}\exp[-D\lambda_n^2(t-t_0)]
\]
(19)
The fits shown by solid lines in Fig. 30 result from Eq. (19). The parameter obtained from the fits is $k_d$, the decay rate in the afterglow of the discharge and determines the loss coefficient of O atoms on the SS surfaces.

C. Variation of decay rates with discharge parameters

To examine the dependence of the parameter $k_d$ on the discharge parameters, we took temporal profiles at widely varying discharge conditions (pressure and power). In Fig. 30, we show two temporal profiles taken in a 3 Torr/50 W and a 0.1 Torr/50 W oxygen discharge, respectively. The high-pressure fit in Fig. 30 (a) is obtained for a loss coefficient $\gamma = 0.6\%$, while the low-pressure fit in Fig. 30 (b) is obtained for $\gamma = 1.3\%$. The increase in the loss coefficient with decreasing pressure is consistent with enhanced ion bombardment at lower pressures.

Fig. 31 shows two more temporal profiles taken in a 0.2 Torr discharge at a power of 55 W and 90 W, respectively. The high-power profile (Fig. 31 (a)) was fit with $\gamma = 1.3\%$, while the low-power profile (Fig. 31 (b)) was fit with $\gamma = 0.75\%$. The increase of the loss coefficient with power is consistent with an enhancement of the ion bombardment (expected at high powers) and it will be shown in detailed data that follow.

Fig. 32 describes in detail the increase in decay rates (in the discharge
Figure 30. Dependence of O-atom decay rates on discharge pressure. Data are fit with $k_d = 86 \text{ s}^{-1}$ (at 3 Torr), and $k_d = 240 \text{ s}^{-1}$ (at 0.1 Torr).
Figure 31. Dependence of O-atom decay rates on discharge power. Data are fit with $k_d = 235 \text{ s}^{-1}$ (at 90 W), and $k_d = 140 \text{ s}^{-1}$ (at 55 W).
Figure 32. Variation of decay rates and the loss coefficient in a discharge afterglow as a function of discharge power.
afterglow) with discharge power. The increase in decay rates is linear with power, possibly since the density of ions bombarding the surface increases linearly with discharge power. The increase of the loss coefficient of O atoms on a SS surface with power, in a 0.2 Torr discharge, is also shown in Fig. 32. The observed increase in $\gamma$ by a factor of 4 for O atoms was not observed in the case of H atoms on a SS surface. As we discussed earlier, a mechanism possibly responsible for the effect is that of enhanced ion bombardment at higher powers which may create more sites for O atoms on the surface, however, this mechanism cannot alter significantly the surface for the more mobile H atoms for which a SS surface represents already a significant sink.

The pressure dependence of the O-atom loss coefficient on a SS surface is demonstrated by means of both, spatial and temporal profiles, as in Figs. 33 and 34. Fig. 33 shows spatial distributions of O atoms obtained in steady state discharges at a pressure ranging from 3 Torr down to 0.25 Torr. We obtained best fits by increasing the loss coefficient of the SS surface from 0.3 % to 1.1 % for the above noted reduction in pressure. We also used temporal profiles to investigate the decay rates for O atoms on a stainless-steel (SS) surface over a wide range of pressures. Fig. 34 shows the variation of the decay rates of O as the pressure decreases from 3 to 0.1 Torr. The solid lines represent the predictions of the diffusion model for the decay rates of O atoms on surfaces.
Figure 33. Spatial profiles of O atoms as a function of pressure indicate a reduction of the loss coefficient of a SS surface from 1.1% to 0.3% as pressure increases from 0.25 Torr to 3 Torr.
with a loss coefficient $\gamma$ over the investigated pressure range. We found that the loss coefficient for O atoms on the SS surface increases from 0.4% to 1.6% as pressure decreases from 3 to 0.1 Torr. A possible explanation for the observed effect is that enhanced ion bombardment at lower pressures where the sheaths get less collisional may create more sites available for O atoms to stick or recombine.

D. Etching plasmas

Because of the technological importance of O atoms in etching plasmas containing fluorine atoms, we measured the decay of O atoms in the presence of fluorine atoms in the discharge. We used a mixture of $\text{O}_2/\text{CF}_4$ at a constant total pressure of 0.2 Torr, and at a total power of 110 W. We varied slowly the composition of the mixture by adding $\text{CF}_4$ to $\text{O}_2$ and we measured the decay rates, as shown in Fig. 35. We observed a significant decrease in the decay rate by about 50% for a small addition ($\approx 5\%$) of $\text{CF}_4$ in the discharge which should not alter the characteristics of the discharge and the diffusion of O atoms, it could however result in competition between O and F atoms to occupy available surface sites. This competition between O and F atoms results in a reduction of the O-atom loss coefficient from 1.45 % to 1.01 % upon 5 % addition of $\text{CF}_4$ in the 0.2 Torr mixture. A more severe effect under addition
Decay rate as a function of inverse pressure.

\[ \gamma = \frac{1.6\%}{P} \]

\[ \gamma = \frac{1\%}{P} \]

\[ \gamma = \frac{0.5\%}{P} \]

\[ \gamma = \frac{0.3\%}{P} \]

**Figure 34.** Decay rates of O atoms in a discharge afterglow as a function of inverse pressure. They indicate an increase of the loss coefficient \( \gamma \) of the surface as pressure decreases.
Figure 35. Reduction of the decay rate of O atoms upon addition of CF$_4$ in a O$_2$ discharge (the total pressure is kept constant at 0.2 Torr).
of fluorinated gases in O\textsubscript{2} discharges had been previously observed by other investigators in CF\textsubscript{4} and SF\textsubscript{6} discharges.\textsuperscript{36,76} We believe that the discharge power at which the experiment is performed affects the outcome of the experiment; when we performed this experiment at a smaller power (55 W) no effect of CF\textsubscript{4} addition on the O-atom loss coefficient could be detected, possibly due to insufficient dissociation of CF\textsubscript{4} that provides fluorine atoms in the discharge.

Finally, we studied the effect of O atoms in a discharge loaded with a photoresist material. We measured the decay rate of O atoms on the photoresist surface by means of a pulsed discharge (110 W, 0.1 Torr) initially and after exposing the material under severe plasma conditions: a high power and low pressure continuous discharge. We observed that, although the material was removed from the surface (evident by the discoloration of the surface on which the photoresist was applied), the decay rate of the O atoms on the surface did not change significantly (a \(\sim\) 10\% decrease was observed). A similar behavior had been observed by Booth et. al.\textsuperscript{76} who reached the conclusion that O atoms are lost at the same rate on both surfaces. However, when we measured the decay rates in a 55 W pulsed discharge, a reduction in \(\gamma\) by about 20-30\% was observed. We believe that this is consistent with the observation\textsuperscript{82} that the chemical character of the photoresist etching vanishes in favor of the mechanical ion-induced effects which prevail in the high ion energy range. Therefore, the
small decrease in $\gamma$ after the photoresist stripping from the surface can be easily obscured by enhanced ion bombardment in high-power discharges.

In conclusion, we determined the loss coefficient for O atoms on electrode surfaces and we found it to vary with the discharge conditions; it increased with decreased pressure, and linearly increased with power. In terms of the composition of the gas mixture, the loss coefficient of O atoms on the electrode surface was found to sharply decrease with a small addition of CF$_4$ in the O$_2$ discharge, possibly due to competition between O and F atoms to occupy available sites on the surface.

E. Rise of the atomic population

The employment of the diffusion model we presented in Chapters III.b and IV.b was very successful in providing fits for the spatial atomic distribution, as well as for the temporal decay of the atomic population in the afterglow of a discharge. By means of this model, the atomic distribution was explained in terms of a time-independent production of atoms in the discharge and heterogeneous losses on the electrode surfaces. However, analysis of temporal profiles in the rise of the discharge and comparison with those in the afterglow (see the profile shown in Fig. 36 for atomic oxygen) reveals a new feature; the rate constant that is needed to describe the rise of the population is
Figure 36. The decay rate for atomic O in the afterglow (t > 2 ms, $k_d = 330 \text{ s}^{-1}$) is much slower than that in the rise (t < 2 ms, $k_r = 1000 \text{ s}^{-1}$).
a lot higher than that of the decay. Specifically, if the rise of the population in Fig. 36 is simulated-at a first approximation-by a single exponential, a rate constant $k_r = 1000 \text{ s}^{-1}$ is necessary, while a much smaller rate constant $k_d = 86 \text{ s}^{-1}$ is necessary for the decay. Note how fast the O-atom concentration would decay if the constant determined from the rise was also used for the decay (triangles).

Certainly, this increase of the rate constant during the discharge cannot not be attributed to an increase in O-atomic losses on the surfaces, since even a loss coefficient $\gamma$ as high as 100% could not accommodate an observed rate of the order of 1000 s$^{-1}$. Thus, we seek other additional mechanisms that may be responsible for the observation.

Certainly, due to the appearance of this additional mechanism in the discharge but not in the afterglow, charged particles could play an important role in it; thus we should examine various possibilities for processes involving ions or electrons. First, ion-molecule reactions involving O atoms were excluded since the ones of interest in this case would be three-body processes and the probability for them to occur would be very small, thus they are not very likely. Second, we investigated the possibility that electron collisions may remove O atoms either from their ground state or from the laser-excited state. Ground-state oxygen atoms are known to be directly excited by electron collisions and cross-sections for these excitations have been calculated.$^{86,78}$
Actually, the actinometric techniques for detection of atomic species by optical emission are based on this process, however the question is whether the effect of direct electron excitation of ground-level atoms is significant enough to result in detectable loss of O atoms in the discharge. If we assume that the rate we measure during the discharge is totally due to direct electron excitation of ground-state atoms, then we determine a cross-section for this process that is at least two orders of magnitude higher than the theoretical calculations even for low-energy electrons. On the other hand, if laser-excited O atoms were quenched by electron collisions during the discharge, this would result to a sharp increase of the LIF signal apparent immediately after the turn-off of the discharge, as charged species that are responsible for the quenching die-off rapidly, thus increasing the yield of the fluorescence. However, such a jump in the LIF signal coincident with the discharge turn-off was not observed in our experiments. We should therefore turn to some other mechanism to explain this observation.

One of the basic assumptions of our model is the time-independent production for atoms, at a rate nearly homogeneous in space for O atoms. However, if one assumes that the production rate decreases as the discharge evolves towards equilibrium, the behavior of the rise of the population could be explained qualitatively. Furthermore, since no significant dissociation was
observed for the investigated discharges, the slowing down of the production rate could not be attributed to the depletion of the parent molecule concentration (O₂ in this case). It is rather evident that one should seek the electron density distribution as a likely candidate. Independent studies in similar discharges have shown that although the electron temperature equilibrates rather rapidly (~μs) on the time scale investigated in these experiments (2 ms), the electron density reaches equilibrium only after 100-200 μs, i.e. a time scale comparable with that of our experiments. We will apply this hypothesis and show that it is consistent with our data since it can lead to the observed increased rates in the rise of the atomic O population and it gives reasonable fits, although we cannot detail the physical causes for the variation in atomic production shortly after discharge initiation.

Since we are interested in simulating the temporal behavior of the concentration measured at a point in space, we could simply include the spatial boundary conditions and the mass transport due to diffusion in a first-order loss term for the atomic concentration ρ(t) of the form -kₐ ρ(t). Then the time-varying concentration should satisfy the equation

\[ \frac{d\rho(t)}{dt} = R(t) - k_a \rho(t) \] (20)

where R(t) is the time-dependent production rate. It is appropriate for this production rate (that is large at small values of t and evolves to a constant value
as time advances) to be approximated by the following function:

$$R(t) = R_0 + R_1 \exp(-k't)$$  \hspace{1cm} (21)$$

where $R_0$ is the steady-state production rate, and $R_1$ is the amplitude of the additional production rate that is exponentially decaying at a rate determined by the electronic density equilibrium time ($k' = 1/\tau \sim 10^4 \, \text{s}^{-1}$). The solution of Eq. (20) is given by

$$\rho(t) = R_0[1-\exp(-k_d t)]/k_d + R_1[\exp(-k_d t)-\exp(-k't)]/(k'-k_d)$$  \hspace{1cm} (22)$$

Temporal profiles taken under various conditions of pressure and discharge power were fit to Eq. (22) with parameters $R_0$ and $R_1$ ($k' = 10^4 \, \text{s}^{-1}$ was used, as suggested in Ref. 77, and $k_d$ was determined by temporal profiles in the discharge afterglow).

In Fig. 37, we show temporal profiles and fits for the rise of the atomic population at the lowest and highest values of pressure used in our experiments (0.1 T, 3 T). For the fit at 3 Torr a value of $R_1/R_0 = 8$ was used, while a value of 2 was used for the fit at 0.1 Torr. The discharge power was also a variable in our experiments, and temporal profiles and fits for the rise of O concentrations at two discharge powers (55 W, 90 W) are shown in Fig. 38. The values used for the ratio of the production rates were $R_1/R_0 = 2$ and 3, at 55 W and 90 W respectively. The variation of the ratio $R_1/R_0$ with pressure and
Figure 37. Dependence of the rise of the O concentration on the discharge pressure. Data and fits suggest a higher production rate ratio $R_i/R_0$ at higher pressures.
Figure 38. Dependence of the rise of the O concentration on the discharge power. Similarly to the pressure dependence, data and fits suggest a higher production rate ratio at higher powers.
power is expected due to the fact that both of these discharge parameters affect
the electron density and the electron collision frequency with O₂.

The fact that the hypothesis for time-dependent atom production was not
evidently necessary to the analysis of H-atom profiles lies in the fact that most
of these profiles were taken over a surface characterized by much more
significant losses for H atoms, resulting in a fast rise behavior comparable to
that due to the time-dependent production rates. Thus, allowing the diffusion
coefficient to vary within ±15% was sufficient to compensate for the time-
independent production, as we assumed for the simulations of the spatial
profiles at various times after the onset of the discharge (see Fig. 15). However,
when surfaces with a small loss coefficient such as Si were used, the
introduction of a time-dependent production rate in the model became
necessary. This is shown in Fig. 39 where the rise of the H-atom concentration
is fit to Eq. (22) with the ratio R₁/R₀ = 6. (In the case of H atoms, the increased
value of the rise rate constant could be accommodated by an increased loss
coefficient γ for H atoms on electrode surfaces during the discharge, due to
increased ion bombardment on the surface. However, the fact that the rise rates
increased with pressure diminishes the likelihood of the latter explanation, since
ion bombardment and thus the surface loss would be expected to be reduced at
higher pressures.)
Figure 39. Temporal profile taken in a 3 Torr H₂ discharge with a Si wafer loaded on the ground electrode. The rise was fit by means of a time-dependent production for H atoms.
Finally, the solution in Eq. (22) for a time-dependent production rate converges at large values of t to the temporal behavior of Eqs. (6) and (15), thus the spatial distribution for H and O atoms at steady-state (t→∞, Figs. 14, 23, 33) is not sensitive to details concerning the production of the atoms during the first 100's μs after the discharge initiation.
CHAPTER V
CONCLUSIONS

Throughout this work, the two-photon allowed laser-induced fluorescence technique (TALIF) was used as an *in-situ* diagnostic to provide information about the spatial and temporal distribution of atomic hydrogen and oxygen in rf discharges. We obtained absolute concentrations for these species that have been proven of great significance in the processing of materials, under conditions similar to those typically found in commercial processing reactors. We have found that, in the presence of various surfaces, the distribution of these species alters in a way characteristic of the surface. For example, surfaces with high reactivity to H or O atoms result in significant concentration gradients adjacent to them. A model assuming diffusion as the dominant mechanism governing neutral distribution describes with good agreement the spatial and temporal distribution of atomic species in the discharge. Detailed estimation of the loss coefficient of H and O atoms on bounding surfaces showed a dependence of the surface characteristics on the discharge conditions (pressure, power, and gas composition). This observation is of central importance since
it establishes *in-situ* techniques as the only reliable way to determine surface properties in reactive environments. Furthermore, a permanent alteration of the surface properties was observed in some cases after treatment of the surface in an energetic plasma (high power/low pressure). Therefore, the TALIF diagnostic technique has been proven a sensitive *in-real time* monitor of plasma-induced processes on surfaces. We believe that this work provides a fundamental picture of the distribution of atomic species in a discharge, and it can be certainly applied to other atomic species for which the TALIF scheme is experimentally feasible, and in reactive environments other than rf discharges, such as in flames or in high-pressure CVD reactors, given the fact that depopulation mechanisms for the laser-excited state (such as quenching\textsuperscript{48,83}) can be accounted for.

Indeed, we have employed the TALIF diagnostic technique for the detection of atomic hydrogen and oxygen in a variety of environments, in our and in collaborating laboratories. Specifically, we have implemented TALIF detection to characterize the H and O-atom concentrations in a commercial (ASTEX) reactor that is used for diamond-film production, under diamond-growth conditions,\textsuperscript{83} in a prototype parallel plate reactor designed and built as a reference reactor for the low-temperature plasma community (GEC Reference Cell,\textsuperscript{84} the particular one is located at Wright-Laboratories),\textsuperscript{85} in an oxy-
acetylene flame used to deposit diamond, and finally in a commercial halogen (GE) lamp, where H atoms were produced by thermally dissociated HBr near a hot filament. In conclusion, the variety of environments where the TALIF technique can be employed to detect atomic species is limited only by imagination. Naturally, special attention is advised to the particular conditions under which each reactive plasma environment functions so that factors that may invalidate the accuracy of the technique (such as SE and quenching of fluorescence) are prevented or taken into account.
APPENDIX

ANALYTICAL SOLUTION OF DIFFUSION EQUATION WITH MIXED BOUNDARY CONDITIONS

The transport of neutral species such as H and O atoms in a gaseous environment can be described by a diffusion equation that is subjected to appropriate boundary conditions (B.C). The specifics of our problem imposed the need to solve a modified diffusion equation that contained a production term for the atomic species, with boundary conditions specified by the nature of the surfaces confining the gaseous environment, namely the electrode surfaces. Since these solid surfaces provide a body for atom removal at some degree, the atomic species concentration at the boundaries is determined by the ability of the surface to sustain a directed flux of particles disappearing onto it and a random flux of those surviving the contact with the wall. Thus, the non-homogeneous diffusion equation (Eqs. (5), (13)) presented in chapters III, IV had to be solved with mixed boundary conditions which combine in one relation both the concentration, \( \rho \), and its gradient \( d\rho/dx \) (as described by Eq. (4)).

Following a typical way for solving non-homogeneous differential
equations, we first seek a general solution for the homogeneous equation:
\[ \frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} \]  
(23)
This can be easily solved by separation of variables if we write
\[ \rho(x,t) = X(x)T(t), \]
and it leads to two differential equations for the spatial and temporal part of \( \rho \), respectively,
\[ \frac{d^2 X}{dx^2} = -\lambda^2 X \]  
(24)
\[ \frac{dT}{dt} = -\lambda^2 DT \]  
(25)
where \( \lambda \) is a constant to be determined such as the solution of Eq. (24)
\[ X(x) = A \sin \lambda x + B \cos \lambda x \]  
(26)
satisfies the boundary conditions of Eqs. (14a) and (14b). The spatial part of the solution must then satisfy the following B.C:
\[ \frac{dX}{dx} = \beta_i X \text{ at } x=0 \]  
(27a)
\[ \frac{dX}{dx} = \beta_2 X \text{ at } x=a \]  
(27b)
where \( \beta_i = (\nu/4D)\gamma_i/(1-\gamma_i) \), \( i=1,2 \) for the boundaries at \( x=0 \) and \( x=a \), respectively. Application of these B.C on Eq. (26) yields the relation that \( \lambda \) must satisfy:
\[ \tan(\lambda a) = (\beta_1 + \beta_2)\lambda / (\lambda^2 - \beta_1 \beta_2) \]  
(28)
If we put
\[ \tan \delta_1 = \beta_1 / \lambda \text{ and } \tan \delta_2 = \beta_2 / \lambda \]
we obtain
\[
\tan \lambda a = \tan (\delta_1 + \delta_2)
\]
or equivalently
\[
\lambda a = \delta_1 + \delta_2 + n\pi = \tan^{-1}(\beta_1/\lambda) + \tan^{-1}(\beta_2/\lambda) + n\pi \quad n=1,2,3,\ldots
\]
This equation is the quantization condition for \( \lambda \) and its roots \( \lambda_n \) were determined numerically in this work. Then, the solution of the spatial equation (26) can be generalized to form an orthonormal set of functions
\[
X_n = (2/a)^{1/2} \cos(\lambda_n x - \delta_n)
\]
(30)
To find the solution of the non-homogeneous diffusion equation
\[
\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} + R_0[\delta(x-x_0) + \delta(x-a+x_0)]
\]
(5)
that describes the transport of atomic hydrogen in the discharge, as we discussed in chapter III, we first conveniently expand the two \( \delta \)-functions in terms of the \( X_n \)'s,
\[
\delta(x-x_0) = \sum X_n(x)X(x_0)
\]
(31)
\[
\delta(x-a+x_0) = \sum X(x)X(a-x_0)
\]
(32)
If we also expand the solution
\[
\rho(x,t) = \sum X_n(x)T_n(t)
\]
(33)
and we substitute it in Eq. (5), we obtain the following differential equation for the temporal part \( T(t) \) of the solution:
\[
\frac{dT_n(t)}{dt} + D\lambda_n^2 T_n(t) = R_0[X_n(x_0) + X_n(a-x_0)]
\]
(34)
The solution that satisfies the initial condition \( T_n(0)=0 \) is
\[ T_n(t) = R_0 [X_n(x_0) + X_n(a-x_0)][1/(D\lambda_n^2)][1-\exp(-D\lambda_n^2 t)] \] (35)

Then the solution for \( \rho(x,t) \) takes the form
\[ \rho_n(x,t) = (2R_0/aD) \Sigma(1/\lambda_n^2) \{ \cos(\lambda_n x_0 - \delta_n) + \cos[\lambda_n(a-x_0) - \delta_n] \} \cos(\lambda_n x - \delta_n) \times \]
\[ \times [1-\exp(-D\lambda_n^2 t)] \] (36)

which was presented in chapter III (Eqs. (6), (7)).

A simplified form of Eq. (36) first appeared in our work in the limits of totally absorbing (\( \gamma = 1, \rho = 0 \)) and totally reflecting (\( \gamma = 0, \frac{d\rho}{dt} = 0 \)) boundaries.\(^{88,89}\) The approximation of a totally absorbing boundary was proven to be a reasonable one for a stainless-steel surface, however the generalized solution (36) provided a more accurate means of determining a loss coefficient \( \gamma \) for atomic hydrogen on a variety of surfaces, and it was routinely used throughout this work.

The diffusion equation that describes the transport of O atoms differs from Eq. (5) for H atoms in the production term (see discussion for O-atom spatial profiles in chapter IV),
\[ R_0(x) = R_0 \int \delta(x-x')dx' \] (14)

where the integral is to be calculated in the range \([x_0, a-x_0]\) which represents the region where O-atoms are homogeneously produced at a rate \( R_0 \).

It is very convenient the fact that we have solved already the problem for atoms produced from two point sources (H atoms), in other words we have
already the Green function of the diffusion equation, and that is
\[
G(x, x', t-t') = \frac{2}{a} \sum \cos(\lambda_n x-\delta_n)\cos(\lambda_n x'-\delta_n) \exp[-D\lambda_n^2(t-t')] \tag{37}
\]
By applying Green's theorem, we obtain the solution for the particular boundary conditions as in Eq. (4), and the initial condition \(\rho(x,0)=0\),
\[
\rho(x,t) = \int G(x,x',t-t')R_0(x')dx' \tag{38}
\]
\[
\rho(x,t) = (2R_0/aD) \sum \frac{1}{\lambda_n^2}\{\sin(\lambda_n(a-x_0)-\delta_n)\sin(\lambda_n x_0-\delta_n)\}\cos(\lambda_n x-\delta_n) \times
\exp[-D\lambda_n^2t] \tag{39}
\]
This is the solution for O-atoms shown in a simplified form in Eqs. (15), (16).

What simplified the solution of these problems was the fact that the concentration \(\rho\) and its gradient were simply related by the loss coefficient in the boundary conditions. Also the assumptions concerning the particle production term were convenient, sufficient however to provide reasonable simulations to our data. Obviously, analytical solutions can be found even with more complicated expressions for the production terms, provided that closed forms exist for the integrated functions appearing in Eq. (38).
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