All sets contained 0.5% by weight NaCl. Analysis of one of the duplicate preparations of each set was done on one day, the other on the following day by ICP-AES using ultrasonic calibration standards containing only 1% nitric acid. F ratios were calculated for each element, and none can be called significantly different at the 5% level of critical values of F.

III. CONCLUSIONS

Inductively coupled plasma-atomic emission spectroscopy has already been shown to be a viable technique for providing rapid, precise, and accurate quantitative analysis of environmental samples. Data presented demonstrate that ICP-AES analytical qualities can be extended, through the use of ultrasonic nebulization, to include analyses requiring ultratrace quantitative data such as EPA's Primary Drinking Water Requirements. Because it can be operated at low carrier flows while maintaining large orifice diameters, the ultrasonic system is superior to the pneumatic system when samples containing solids are to be analyzed. Data shown here (Table VII) indicate that a portion of the particulate or adsorbed sample material is transported by the ultrasonic nebulizer to the plasma torch and detected. Using the proposed method, titanium was not detected using a pneumatic system but was found by using an ultrasonic system and injecting the unfiltered sample. Analysis of these unfiltered samples could not be accomplished using a pneumatic nebulizer because of plugging problems.

Priority pollutant metals analysis by ICP-AES using the ultrasonic system was not affected by the presence of organic pollutants (humic acid 9 ppm, fulvic acid 5 ppm) and moderately high salt concentrations (0.5 wt % NaCl), both of which are often found in environmental waters. While sample types reported here were analyzed using ICP-AES and ultrasonic nebulization, no plugged nebulizers were encountered, no interferences due to desolvation were observed, and no new problems with sample memory were observed. Required rinse times between analyses for both ultrasonic and pneumatic systems are dependent upon sample characteristics rather than on the nebulization system and for the sample types discussed here, rinse times were found to be the same for either system. Briefly, the two systems do not change ICP-AES analysis time requirements, but the ultrasonic system will provide more desirable detection limits and is more trouble free when nebulizer plugging is a problem.

ACKNOWLEDGMENT

The samples containing organic acids and salt were kindly supplied by Donald E. Leyden, Department of Chemistry, University of Denver.

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Evaluation of Silicon-Chemiluminescence Monitoring as a Novel Method for Atomic Fluorine Determination and End Point Detection in Plasma Etch Systems

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Optical methods for the detection of atomic fluorine in plasma etch systems are discussed and an experimental comparison is made between detection by optical emission and by a novel method based on the chemiluminescence from solid silicon in the presence of atomic fluorine. Although both methods are, in principle, subject to interferences, they can readily be used for plasma etch process optimization and for end point detection.

Index Headings: **Atomic fluorine detection; Etch end point detection; Chemiluminescence.**

INTRODUCTION

In plasma etching of semiconductor materials, such as polysilicon, silicon dioxide, and silicon nitride, gas mixtures containing fluorine are used widely. In discharging these mixtures atomic fluorine is produced among other species. The atomic fluorine has a strong reactivity towards silicon and is also relatively long lived. Since the performance of fluorine-based plasma etch processes depends on the amount of atomic fluorine present in the plasma, a means of determining the (relative) atomic fluorine concentration would be helpful in the optimization of the plasma etch processes. If this concentration is monitored continuously, end point detection of those

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plasma etch processes that mainly involve reactions of atomic fluorine with the substrate is possible as the end point is accompanied by a change of the F atom concentration.

The detection of atomic fluorine in plasma etch systems has thus far been performed by optical titration with chlorine[1] and by atomic emission spectrometry.[2,3] Recently, a novel technique has also been suggested based on the detection of the luminescence that arises from the interaction of fluorine atoms with silicon.[4]

In this paper the principles of each of the above mentioned optical techniques are discussed and an experimental comparison is made between the monitoring of the optical emission and of the luminescence as tools for the study of plasma etch processes and for the detection of the end point of etching.

I. METHODS

A. Luminescence. The occurrence of a chemiluminescence near a silicon surface was reported earlier by Horiike and Shibagaki[5] for a CF_4-O_2 plasma. Recently, the chemiluminescence was analyzed in more detail.[4] It was found to be the sole result of the interaction of atomic fluorine with silicon. The luminescent intensity was given by the relation:

$$I_{\mathrm{lum}} \alpha [\mathrm{F}]^2 \quad (1)$$

Thus, the monitoring of the luminescence would provide a means for continuous detection of atomic fluorine. In many cases atomic fluorine is most efficiently produced if some oxygen is added to the plasma gas, e.g., CF_4, SiF_4, or SF_6. Then, at low-oxygen concentrations almost all oxygen is consumed by the plasma, but at higher concentrations excess oxygen may be present.[1,6] This excess oxygen may lead to various interferences, which disturb the intensity relation given above. Firstly, a spectral interference at 762 nm due to emission from metastable oxygen molecules occurs.[4,7] Secondly, excess oxygen results in a relative enhancement of the intensity in the ultraviolet part of the spectrum.[4] If atomic fluorine is to be monitored at variable oxygen concentrations, the intensity relation [Eq. (1)] consequently is not strictly obeyed. Because the intensity of the luminescence is low compared to the optical emission from the plasma itself, atomic fluorine concentrations can only be determined at a position that is optically separated from the plasma, e.g., the pump exhaust line. Thus, reactions of atomic fluorine with oxygen[6,8] may take place in the region between plasma and the luminescing silicon substrate, also disturbing the intensity relation if the oxygen concentration is taken as a variable. On the other hand, the quadratic dependence of intensity on concentration may permit sensitive detection of changes in concentration. In addition, the integral intensity can be monitored, resulting in light output signals that can be detected with a low-cost photodiode detection system.

B. Optical Emission from Excited Fluorine Atoms. The monitoring of the optical emission from excited atomic and molecular species has been used most widely for end point detection.[2,3] For atomic species the line intensity is proportional to the concentration if dissociative excitation processes of the molecule into excited atomic species can be neglected with respect to direct excitation of the atom. Although this is usually the case, there are some important exceptions. The oxygen molecule has several metastable states near its dissociation limit,[9] so that for this molecule formation of excited atomic species in the plasma by dissociative excitation from the metastable state cannot be ruled out *a priori*. Another exception is found if helium is added to the plasma. Because of the high metastable energy of that atom,[10] dissociative excitation processes may dominate and, as a result, a direct relation between atom concentration and line intensity is lost.[11]

For plasmas containing fluorine the $3s^2P$-$3p^2P^0$ transition of the fluorine atom at 703·7 nm is used, because of its high transition probability. The intensity in emission is given by:

$$I_{\mathrm{em}} = \alpha[\mathrm{F}] \quad (2)$$

In this expression α is a proportionality constant whose magnitude depends on electron number density and electron temperature and hence on gas composition.

Interferences may occur from nearby spectral lines. Use of broadband filters to obtain high light output signals has therefore to be paid for by the occurrence of spectral interferences.

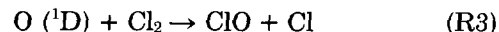
C. Gas Phase Titration. Atomic fluorine can be detected by an optical gas phase titration reaction with chlorine:[1,12]

$$\mathrm{F} + \mathrm{Cl_2} \rightarrow \mathrm{FCl} + \mathrm{Cl} \quad (\mathrm{R1})$$

$$\mathrm{Cl} + \mathrm{Cl} \rightarrow \mathrm{Cl_2}^* \quad (\mathrm{R2})$$

The chlorine luminescence at wavelengths longer than 600 nm is detected downstream from the Cl_2 injection point. Raising the quantity of added chlorine to an atomic fluorine-containing gas mixture increases the luminescent intensity until all atomic fluorine is consumed by reaction (1). Consequently the method can be used to determine absolute F concentrations.

Interferences with reaction (1) may occur such as is the case when oxygen is present in the plasma gas. If the distance between chlorine injection point and plasma is not sufficiently large, O (^{1}D) atoms are present in the plasma exhaust and these atoms also react with chlorine:



$$\mathrm{O}\ (^1\mathrm{D}) + \mathrm{Cl_2} \rightarrow \mathrm{ClO} + \mathrm{Cl} \quad (\mathrm{R3})$$

leading to additional formation of excited chlorine by reaction (2). The rate constants for reactions (1) and (3) are equal within the accuracy of their determination.[13,14] Additionally, spectral interferences may occur from emission of metastable oxygen molecules.[7]

If the method is to be used for continuous monitoring of atomic fluorine, as required for end point detection, care has to be taken that excess chlorine is always added. In a production environment, however, the use of this gas should be avoided if possible. Moreover, the chlorine may produce extra pump oil degradation.

Thus, as a whole, the monitoring of the silicon luminescence and the optical emission from excited fluorine appear to be the most practical to use. We have therefore made a comparison between these two methods only. Because of the different dependence of optical emission intensity and luminescent intensity on atomic fluorine concentrations [Eqs. (1) and (2)], the square root of the

luminescent intensity will be compared with the optical emission intensity throughout to describe relative levels of atomic fluorine concentrations.

II. EXPERIMENTAL

The experimental set-up is shown in Fig. 1. It consists of a 6 in. by 13 in. barrel reactor (IPC) with a perforated aluminium tunnel inside. Radio-frequency (rf) power (13.56 MHz, 100 to 150 W) is capacitively coupled to the plasma via a matching network. Gas pressures (100 to 160 Pa) were determined with a capacitance manometer.

The chemiluminescence of a 1-in. diameter silicon wafer, which was placed in the pump exhaust line at a distance of 20 cm from the reactor outlet, was measured via a quartz window with an uncooled Philips XP 1002 photomultiplier tube. An optical separation from the plasma was obtained by bending the pump exhaust line twice between the silicon wafer and the reactor.

The optical emission between the reactor wall and the perforated aluminium tunnel in the region near the pump exhaust was observed in the axial direction through a quartz window at the front of the reactor. By means of a UV optical conductor the plasma emission was directed to the entrance slit of a 0.25-m Jarrell-Ash monochromator equipped with a grating blazed at 600 nm. Slit widths of 50 and 500 μm gave an instrumental resolution of 0.35 and 3.5 nm, respectively. The light emission was detected at the exit slit with a thermoelectrically cooled photomultiplier tube (RCA C31034).

Thermally oxidized silicon wafers of 2-in. diameter covered on both sides with undoped low pressure chemical vapor desposition (LPCVD) polysilicon (4800 Å) were used. The wafers were unmasked. Absolute etch rates of polysilicon were determined by thickness measurements using a reflectometer.

III. RESULTS AND DISCUSSION

A. Reactor Conditioning. Fig. 2A shows the behavior of I_{em} and $I_{lum}^{1/2}$ as a function of time after a plasma in CF_4-7% O_2 has been initiated. Apparently, I_{em} and $I_{lum}^{1/2}$ exhibit the same behavior; this figure indicates that almost ½ h is required to reach a situation in which a steady atomic fluorine concentration is obtained in the reactor. In Fig. 2B the effect of preheating the reactor for 10 min with a N_2 plasma is indicated. During the preheat cycle the temperature of the reactor increases to 140°C and consequently we increased the pump exhaust

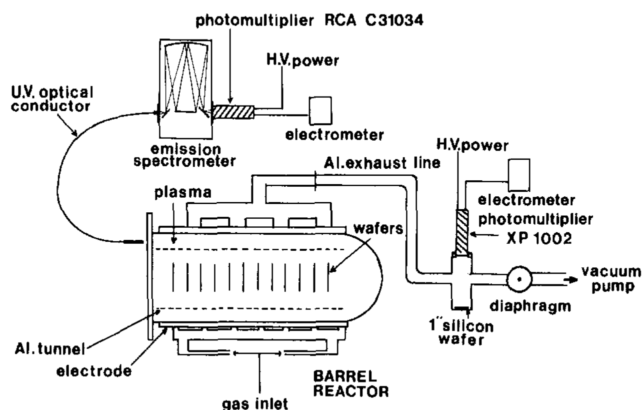


FIG. 1. Schematic diagram of the experimental setup.

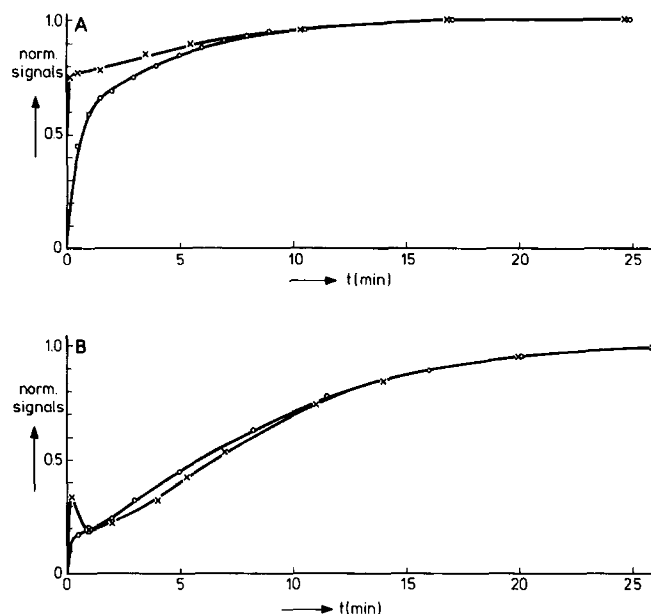


FIG. 2. A. Conditioning of an unloaded reactor at room temperature. Normalized I_{em} (×——×) and $I_{lum}^{1/2}$ (O——O) vs time. Conditions: CF_4-7% O_2 gas mixture, flow rate 375 std cm^3/min, pressure 130 Pa, and rf power 100 W. B. Conditioning of an unloaded barrel reactor at 140°C. Temperature pump exhaust line 140°C. Other conditions: see A. Normalized I_{em} (×——×) and $I_{lum}^{1/2}$ (O——O) vs time.

line to the same temperature by means of external electrical heating. After preheating, the fluorine atom line emission signal stabilizes within 15 s, whereas the luminescence reaches a steady signal after only a few minutes. This longer time required for the luminescent signal is probably not related to the conditioning of the reactor, but rather to a recovery time of the silicon surface from which the luminescence is observed. This was checked by switching off the rf power for 1 min after the luminescence was stabilized. The luminescence intensity then reached its original value after a period of several minutes. The reason for this long recovery time of the luminescence is not yet properly understood.

B. Effect of Oxygen Addition to CF_4. It is known that the addition of small quantities of oxygen to a CF_4 plasma strongly enhances the decomposition of CF_4 into atomic fluorine, resulting in an enhanced etch rate of Si and SiO_4.[1, 6] Therefore, the luminescent and the emission signals will also depend on the oxygen concentration in the plasma feed gas. This is shown in Fig. 3 for an unloaded reactor. The oxygen flow was varied, while the CF_4 flow rate and the pumping speed were maintained constant; as a consequence the pressure varied between 130 and 160 Pa in the range from 0 to 25% added oxygen. Obviously, the emission signal has its maximum at a higher oxygen content than the luminescence. Fig. 3 also shows that under the conditions prevailing in the barrel reactor the etch rate of polysilicon as a function of the oxygen content follows the optical emission signals rather than the atomic fluorine concentration as determined from the luminescence of silicon.

The fact that the luminescence does not fully reflect the etch rate could be traced back to the limited pumping speed of our system, which results in a decrease of atomic fluorine concentration between reactor and observation region of the luminescence as a consequence of reactions

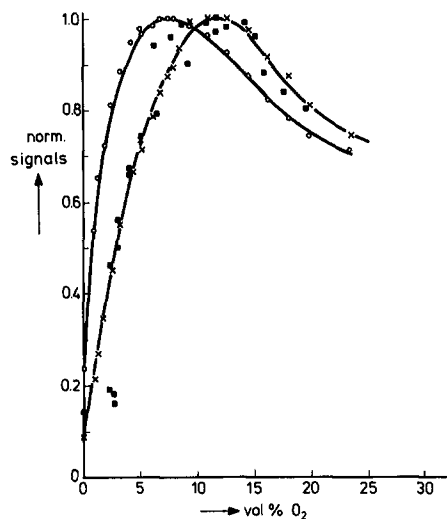


FIG. 3. The normalized I_{em} (×——×), $I_{lum}^{1/2}$ (○——○) and the etch rate of polysilicon (■—■—■) vs O_2 concentration in the feed. Etch conditions: flow rate CF_4, 350 std cm^3/min; rf power, 100 W. gas pressure, 130 to 160 Pa.

with ground-state molecular oxygen in the pump exhaust line.[4, 6, 8] This was concluded from two different experiments.

In the first experiment the pumping speed was varied, while the reactor pressure was maintained constant (130 Pa). When the pumping speed was decreased it was found that the maximum of the atomic fluorine emission intensity was intensified and shifted to higher oxygen concentrations (Fig. 4). For the luminescent signals the position of the maximum is relatively unaffected by the pumping speed and, contrary to the emission signals, the intensity of the luminescence at the maximum decreased again at the lowest pumping speed used. These results are explained as follows. At longer residence times the plasma decomposition of the CF_4 will become more efficient. This implies that more oxygen can react with the CF_4 plasma decomposition products yielding atomic fluorine.[1, 6] Thus, at longer residence times the concentration of atomic fluorine will increase and at the same time the maximum of the concentration will shift to higher oxygen contents of the plasma feed gas. This becomes directly apparent in the optical emission signals. In the case of the luminescence, however, the effect of increasing the residence time is an increased deactivation of atomic fluorine by reactions with excess oxygen in the pump exhaust line. These more or less balance the increase of F production in the reactor. As a result, the position of the maximum of the luminescence and its intensity is much less sensitive to the pumping speed than is the optical emission. In Fig. 4 it is observed that at very long residence times the reactions in the pump exhaust line cause even an apparent decrease of the atomic fluorine concentration.

It is expected, therefore, that the luminescence would increasingly relate to the concentration of atomic fluorine in the reactor, if these reactions became less important, as would be the case when operating at higher pumping speeds and lower pressures. This was checked in a different type of afterglow etcher described before,[6, 15] which has a pumping speed of 450 liters/min and operates at 30 Pa. Briefly, the system consists of a microwave discharge whose effluent is pumped into a reactor. Inside this reactor a 3-in. silicon wafer is placed close to a mass spectrometer head, allowing us to measure the relative amounts of atomic fluorine by monitoring the concentration of the main etch product SiF_4. At the same time the amount of atomic fluorine is monitored from the luminescence of a silicon rod in the pump exhaust line. The dependence of both signals on oxygen concentration for a CF_4-O_2 plasma at a microwave power of 150 W, a CF_4 flow rate of 115 std cm^3/min and a fixed total pressure of 30 Pa are shown in Fig. 5. It appears that under these conditions there is a good correlation between the atomic fluorine concentration in the reactor and that in the pump exhaust line. Only after the maximum does the square root of the luminescent intensity deviate slightly from the SiF_4 production owing to the relative increase of the luminescent intensity at the short wavelength side of the spectrum if excess oxygen is present.[4]

C. End Point Detection. The etching experiments for the evaluation of the luminescence and the emission monitoring as tools for end point detection were performed in a CF_4-16% O_2 mixture at 100 Pa and a rf power of 100 W. Before the etching a preheat cycle with an N_2 plasma at 130 Pa and a rf power of 150 W was applied.

Fig. 6 shows the behavior of I_{em} and I_{lum} during the etching of seven thermally oxidized wafers, the surface of which were covered with 0.5 μm polysilicon. The follow-

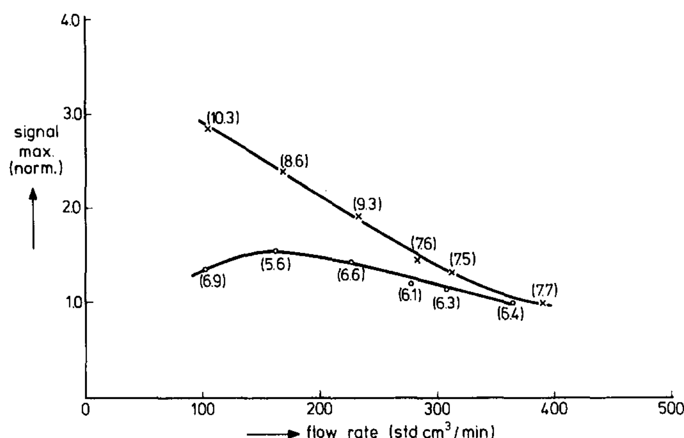


FIG. 4. Maximum intensities of I_{em} (×——×) and $I_{lum}^{1/2}$ (○——○) normalized, vs total flow of CF_4-O_2 using a rf power of 100 W and a pressure of 130 Pa at variable O_2 concentrations. Oxygen percentages in the feed are indicated in parentheses.

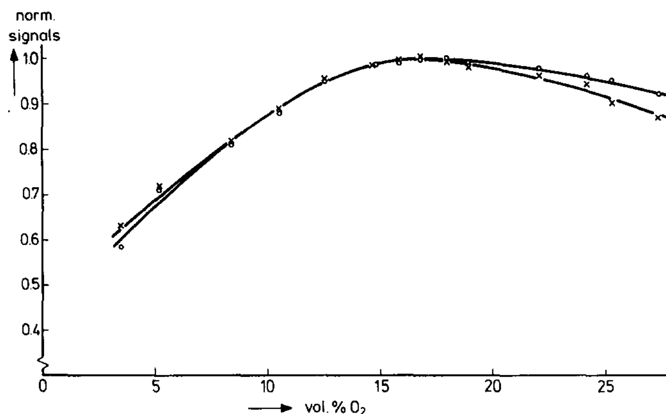


FIG. 5. Normalized $I_{lum}^{1/2}$ (○——○) and SiF_4 production (SiF_3^+, 85 amu, ×——×) vs O_2 concentration in the feed.

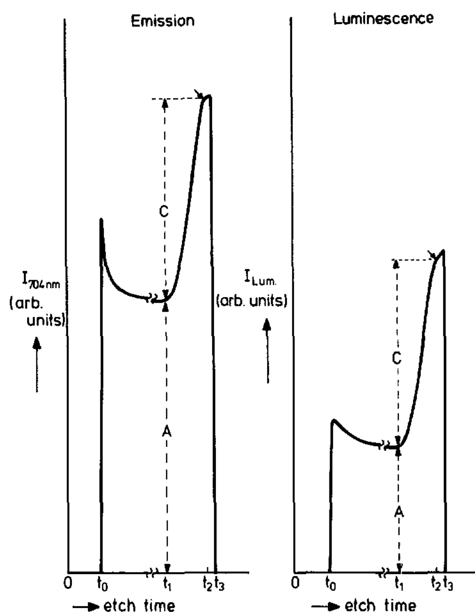


FIG. 6. Signal intensities I_{lum} and I_{em}, etching seven wafers at 100 Pa, 100 W and a total flow of 220 stdcm^3/min, after preheating. t_0, rf power on, start etching polysilicon, t_1, polysilicon etching finished at the edges of the wafers, t_2, polysilicon etching completed, etching SiO_2; t_3, rf power off.

ing was observed: (a) Both signals start to increase at the same time (t_1). At this moment etching of the oxide layer starts to occur; (b) The change of the luminescent signal is larger, as is expected on the basis of the quadratic dependence of luminescent intensity on atomic fluorine concentration; (c) The point at which all polysilicon has been etched away, t_2, is more difficult to detect with the luminescence method than with the optical emission method. This is related to the earlier mentioned long recovery time of the luminescent signals.

The last observation implies that good etch homogeneity is required if the luminescence method is to be applied. This, however, is already a prerequisite for etch processes. Preliminary experiments have indicated that the luminescent intensity is sufficiently high to allow for detection with a photodiode system. Moreover, interference filters are not required. Thus, the luminescence monitoring constitutes a relatively simple and low-cost end point detection system for etch processes based on atomic fluorine reactions and can also be used in etch systems in which plasma and reactor are at a remote distance.

We found that the near end point behavior of both the luminescence and the emission can be described by a simple model, on the assumption that the only etching species is atomic fluorine and that the generation rate of atomic fluorine, G, is not affected by the material being etched. The number of fluorine atoms produced per unit time is then given by:

$$\frac{d\,[\mathrm{F}]}{dt} = G - L\,[\mathrm{F}] - \gamma nOR \qquad (3)$$

which under steady-state conditions leads to:

$$[\mathrm{F}] = \frac{G - \gamma nOR}{L} \qquad (4)$$

In these expressions L represents the pumping speed and n the number of wafers on which a surface area O is being etched at an etch rate R. γ is a proportionality constant. At the end point of the etching of polysilicon a change $\Delta[\mathrm{F}]$ in the atomic fluorine concentration will occur, given by:

$$\Delta[\mathrm{F}] = \frac{\gamma nO}{L} R_{\mathrm{poly}} \left(\frac{S-1}{S}\right) \qquad (5)$$

where the selectivity S is defined as the ratio of polysilicon and silicon oxide etch rate.

If A is the signal during the etching of polysilicon and C the change of signal at the end point, then:

$$\Delta[\mathrm{F}] \alpha\ C \qquad (6)$$

for the emission, and

$$\Delta[\mathrm{F}] \alpha\ (A + C)^{1/2} - A^{1/2} \qquad (7)$$

for the luminescence.

Thus, a plot of C or $(A + C)^{1/2} - A^{1/2}$, as the case may be, vs the product of etched area (nO) and etch rate (R_{poly}) would give a straight line through the origin. R_{poly} was determined from the time difference $t_1 - t_0$ and was found to behave in conformity with the known equation for the loading effect.[16] Fig. 7 shows that the signals indeed follow Eqs. (5) to (7), which in turn supports the assumptions made in the derivation of Eq. (3).

IV. CONCLUSIONS

Both the monitoring of the optical emission from excited fluorine atoms and the monitoring of the luminescence from solid silicon yield information on atomic fluorine concentrations in plasma etch systems. With the CF_4-O_2 gas mixture used in this study the luminescent signals are disturbed by reactions taking place between atomic fluorine and molecular oxygen in the pump exhaust line. This interference becomes more severe at lower pumping speeds and higher pressures. On the other hand, the optical emission was found to follow the behavior of the etch rate as a function of oxygen concentration in the plasma feed gas.

Both methods can be used for end point detection. The luminescence signals are much higher allowing the use of cheaper light detection systems than in the optical

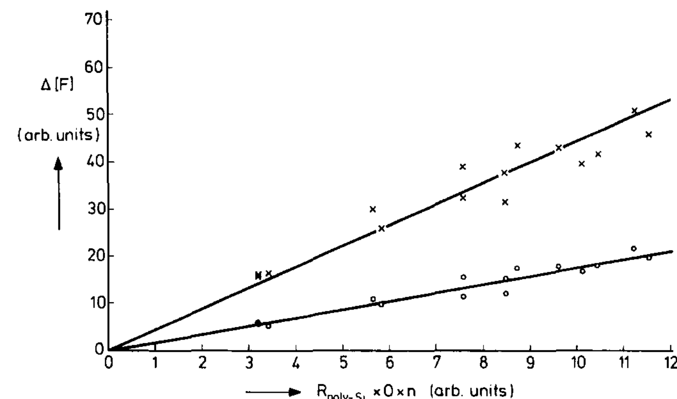


FIG. 7. Change in fluorine concentration, $\Delta[\mathrm{F}]$, being equal to C and $(A + C)^{1/2} - A^{1/2}$ for emission and luminescence, respectively, at the end point of etching polySi on SiO_2 vs momentary etched volumes.

emission method. However, due to the long signal recovery time it can be used only if the etching is sufficiently homogeneous. Moreover, the method can also be used if the etching is to be done in systems for which the plasma chamber is at a remote distance from the reactor and then is less cumbersome than optical titration with chlorine.

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Nature of the Carbonyl Stretching Modes in α-Dicarbonyl Compounds—The Pyruvate Series

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The infrared and Raman spectra in the carbonyl stretching region have been recorded for a number of molecules of the pyruvate series. The data are compared with previously published data for the oxalate series. Analysis of these spectra indicates that there is little or no electronic interaction between the two unsaturated centers. It is therefore concluded that each carbonyl stretching mode in the infrared spectra of the pyruvate series reflects its own particular functionality.

Index Headings: **Infrared spectra; Pyruvate molecules.**

INTRODUCTION

The electrical interaction that occurs when olefinic carbon-carbon bonds are conjugated with other unsaturated centers is well understood and its effect on the spectral properties of molecules has been widely studied. Molecules in which the two conjugated centers are carbonyl groups (α-dicarbonyl compounds) have not been widely studied, however, and the nature of the interaction between such groups has not been considered in any detail, leading to mostly speculative comments in the literature. This is, no doubt, due to the paucity of spectral information available on molecules of this type. Bellamy[1] reports that there appears to be no interaction between the carbonyl stretching modes of α-diketones, but the conclusions have been drawn from a few, relatively complex molecules.

The only other reported data are for molecules of the oxalate series. A number of oxalate molecules have been studied in detail, but the data are scattered rather widely throughout the literature. Nearly all of these molecules possess a center of symmetry and so the mechanical interaction between the two carbonyl groups would be expected to be fairly large. In addition, the center requires that in their normally more stable structure (trans, planar) one carbonyl stretch is Raman active and the other infrared active. Little attention has been paid to possible electronic interactions in these molecules.

As a part of a study of biologically significant small molecules we have studied the spectra of a number of molecules of the pyruvate series. These molecules furnish other examples of α-dicarbonyl compounds, but in which the two carbonyl groups have a different functionality. Comparison of the data in the carbonyl stretching region with those reported for the oxalate series allows conclusions to be drawn concerning the nature of the interaction between the two carbonyl groups in α-dicarbonyl compounds which are of a more general nature than was previously possible. It is concluded that there is very little, if any, electrical interaction between the two carbonyl groups in the ground electronic states of α-dicarbonyl compounds. The results can be readily interpreted in terms of mechanical coupling only.

I. EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer model 180 infrared spectrophotometer. The spectra of those compounds which are solid at room temperature were recorded as Nujol mulls while the spectra of those compounds which are liquid at room temperature were recorded as liquid films. In addition, the infrared spectra of all compounds except pyruvaldehyde were recorded at a nominal temperature of 20 K using a CTi model 20

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