QUENCHING OF THE CHEMILUMINESCENCE PRODUCED BY THE REACTION OF ATOMIC FLUORINE WITH SILICON

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ABSTRACT

The pressure dependence of the intensity I and the spatial distribution D of a characteristic chemiluminescence observed near silicon during etching with atomic fluorine were investigated. The addition of N2 or He to the effluent of a He-5% F2 plasma slightly reduced the etch rate R of silicon and caused a fair reduction of I and D, while addition of small amounts of O2 reduced R and I drastically and hardly affected D. This behaviour can be explained by assuming production of the chemiluminescent species at the silicon surface followed by gas phase quenching.

1. INTRODUCTION

Recent studies$^{1,2,3)}$ have dealt with the origin of the characteristic chemiluminescence CL produced near a silicon substrate during etching with atomic fluorine; the broad featureless continuum extends from about 300 to 800 nm and shows a spatial distribution D, meaning that at least part of it emanates from the gas above the sample and that the lifetime of the CL species or their precursors is relatively long. At constant pressure p, the intensity I of the CL is proportional to the square of the pressure of the SiF_4 produced during etching ($[SiF_4]$) and D shows no dependence on $[SiF_4]$ $^{2)}$. Although it seems well established that the CL species only consists of silicon and fluorine atoms, their precise composition has not yet been determined. Different opinions have been put forward about this composition as well as about the production area of the CL species $^{2,3)}$. It is the object of this contribution to provide additional evidence for the earlier conclusions $^{2)}$ that the CL is due to a single molecular species and that these CL molecules are produced at the etching silicon surface.

2. EXPERIMENTAL

The experiments were performed with the aid of the equipment described before $^{2)}$, using 3" <100> and <111> silicon wafers. The CL and its spatial distribution D were observed parallel and perpendicular to the etching silicon surface. The spectral sensitivity of the optical equipment was carefully calibrated, permitting good comparison with other published calibrated spectral distributions as well as the determination of absolute quantum yields.

3. RESULTS

3.A. Spectral distribution

The normalized absolute spectral distribution of the CL is shown in Fig. 1.

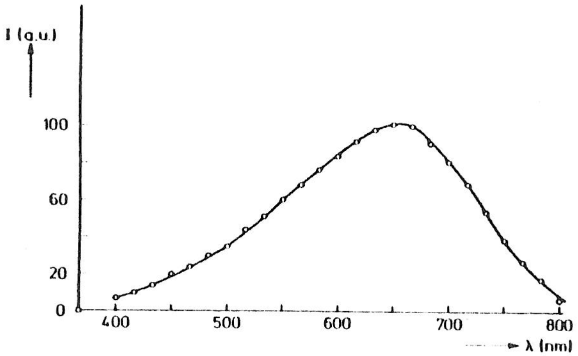

Fig. 1. Normalized spectral distribution of the chemiluminescence, calibration units W/nm.

At the highest resolution of 0.5 nm used, the spectrum preserved its continuous appearance. Apart from a slight difference in peak position, the spectrum closely resembles that of ref. 3. In addition to the previously reported 2) insensitivity of the spectral distribution to the pressure of atomic fluorine and the addition of gases like F_2, N_2, He, CF_4, CO_2 and undischarged O_2, we now also observed independence of it on the silicon temperature T between 325 and 475 K and p between 30 and 130 Pa.

3.B. Intensity

3.B.1. As a function of [F] at constant p

Previously 2) it was observed that I is proportional to $[SiF_4]^2$. In order to relate $[SiF_4]$ and thus I directly to the [F] and the etch rate R of silicon we have simultaneously determined [F] , by comparing mass spectrometer (m.s.) signals of F_2 in the presence and the absence of a plasma, the $[SiF_4]$, by minotoring the m.s. signals at 85 amu, and R, by using an Alphastep. Within 5% both R and $[SiF_4]$ were linearly proportional to [F] . Hence

$$I \propto [F]^2 \text{ and } I \propto R^2. \qquad (1)$$

The latter relation enables the CL, for example, to be used as an etch rate monitor4). The m.s. studies showed that SiF_4 was the main etch product and that other Si_xF_y molecules were formed at concentrations at least 10^{-2} times lower.

3.B.2. As a function of p at constant [F]

a. Addition of "neutral" gases

N_2 or He were added to the effluent of a plasma in He-5% F_2 etching silicon, up to a total p of 133 Pa. The flow rate of He-5% F_2 was fixed at 200 sccm, leading to a base p of 33 Pa. The [F] remained almost constant (a decrease of about 10% for He and about 30% for N_2) while I decreased substantially. The data, corrected for the slight decrease in [F] and normalized to the I of the base mixture I_o are shown in Fig. 2.

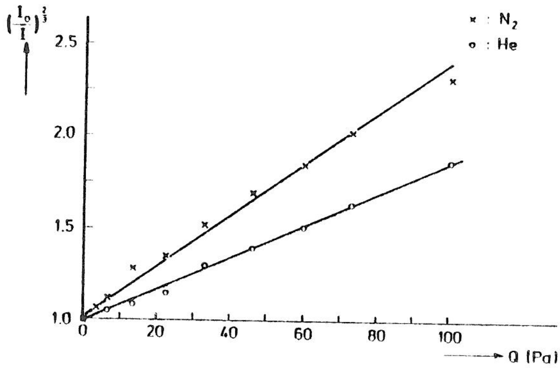

Fig. 2. $(I_o/I)^{2/3}$ as a function of Q, for Q = He or N_2, added to the effluent of a plasma in 33 Pa He-5% F_2 etching Si.

They obey the relation

$$(I_o/I)^{2/3} \propto [Q] \qquad (2)$$

where [Q] is the pressure of N_2 or He added. Evidently, this addition quenches the CL and the quenching is stronger for N_2.

b. Addition of O_2

It can be seen in Fig. 3 that O_2 has a much stronger quenching effect than N_2.

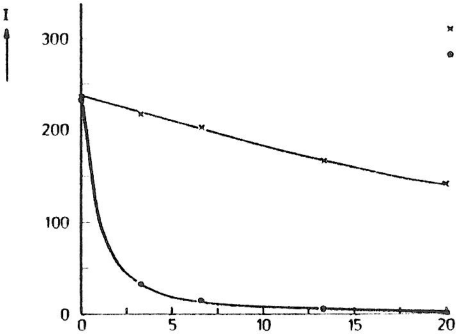

Fig. 3. The same as Fig. 2 for I as a function of N_2 or O_2 added.

Furthermore the relation between I and $[O_2]$ is different from eq. (2). Fig. 4 shows this relation for small amounts of O_2 added to the same base mixture as used in section 3.B.2.a.

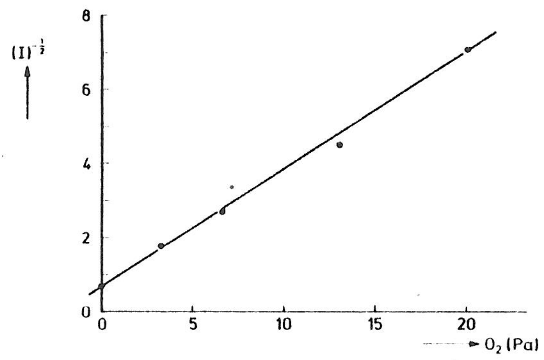

Fig. 4. The same as Fig. 2 for $(I)^{-1/2}$ as a function of O2 added.

It appears that

$$(I)^{-1/2} \propto [O_2] \quad , \qquad (3)$$

where O_2 is the pressure of O_2 added. The addition of O_2 also caused a significant reduction in F and a corresponding increase in F_2 .

3.C. Spatial distribution D of the CL

As published before 2), the D of the CL did not depend on [F] at constant total p. However, D increased clearly with decreasing total p and vice versa.

3.D. Concentration of the CL species [CL]

When the pressure of the effluent of a plasma in He-5% F_2 is reduced from 130 Pa to lower values, I increases up to a maximum which is reached at 20 Pa. Further reduction of p also reduces I. Measurements at the optimum I show that the [CL] relative to [SiF_4] is a fraction of 10^{-6} to 10^{-5}.

4. Discussion

The evidence presented in section 3.A underlines the previous conclusion2) that the CL is due to a single excited $Si_xF_y^*$ species.

M.s. studies of the molecules formed during etching of Si with F show that x = 1 or 2; since $I \propto [F]^2$, it follows that $y \geq 2$; SiF_4 and Si_2F_6 do not possess electronic transitions leading to visible luminescence; F_2^* was excluded previously 2). This leaves us with the possibilities x = 1, y = 2 or 3 and x = 2, y = 2,3,4,5. Further studies will be needed to determine the precise composition of the $Si_xF_y^*$ molecule responsible for the CL.

As stated previously 2), the constant D at constant p, but variable [F] is one piece of evidence for formation of $Si_xF_y^*$ on the Si surface. The discussion of the effects of addition of N_2, He and O_2 to follow below, underline this earlier conclusion. The effect of N_2 and He on I can be readily explained assuming formation of $Si_xF_y^*$ molecules on the etching Si surface; at least part of the $Si_xF_y^*$ leave the Si surface and luminescence or are quenched in the gas phase:

$$Si_s + F_y \xrightarrow{k_1'} Si_xF^*_{y,s} \xrightarrow{k_1''} Si_xF^*_{y,g} \qquad (R1)$$

$$Si_xF^*_{y,g} \xrightarrow{k_2} Si_xF_{y,g} + h\nu \qquad (R2)$$

$$Q + Si_xF^*_{y,g} \xrightarrow{k_3} Q + Si_xF_{y,g} \qquad (R3)$$

where Q represents the pressure of N_2 or He added and k_1 $(= k_1'k_2'')$, k_2 and k_3 are the rate constants of the above reactions. Since $[Si_xF_y^*] \propto [F]^2$, this and the above-given observations and assumptions lead to

$$I = k[F]^2/(k_2 + k_3Q)^{3/2}, \qquad (4)$$

where $Q = [Q]$ and where I is integrally observed perpendicular to the silicon surface. Introduction of I_0 for $Q = 0$ and rearranging yields

$$(I_0/I)^{2/3} = 1/k_2^{1/2} + (k_3/k_2^{3/2})Q, \qquad (5)$$

which is indeed the dependence observed; see equation (2). The different effect of the addition of O_2 on I appears to be quantitatively related to O_2-induced dimerization of F to F_2 via the reactions

$$F + O_2 \xrightarrow{M,W} FO_2 \qquad (R4')$$

$$FO_2 + F \longrightarrow F_2 + O_2 \qquad (R4'')$$

leading to

$$[F] \propto \frac{1}{1+k_4[O_2]}, \qquad (6)$$

a relation formerly observed to be responsible for the reduction of R by a slight excess of O_2 5). Since $I \propto [F]^2$, this results in

$$(I)^{-1/2} \propto 1 + k_4[O_2], \qquad (7)$$

the relation observed in the experiments; see equation (3). In agreement with the relatively small amount of O_2 added in the experiments depicted in Fig. 4, the D only slightly shrunk.

5. REFERENCES

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