SPECTROSCOPIC ANALYSIS OF SiF₄-O₂ MICROWAVE DISCHARGES.

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Summary.

Emission spectra of microwave discharges in SiF₄, O₂ and SiF₄-O₂ mixtures were measured in the range of 850-200 nm. In the SiF₄ and O₂ spectra so far unidentified bands were observed. From the spectra it could be concluded that addition of small amounts of SiF₄ and O₂ have great influence on the spectra of the O₂ and SiF₄ discharges respectively. As a possible explanation for this remarkable change in the spectra the O₂⁺(a¹Σ⁺) excited state is considered.

Introduction.

In most plasma activated deposition processes reaction mechanisms are still obscure although some attempts have been made to reveal essential reaction paths (KAM82, MAT81, COUB1, BREB1, TUR80, MAN83). The complexity of the processes in plasmas makes studies of these reaction mechanisms very difficult. Most studies concentrate on the properties of the deposited layer or material (KUP80, KOE75, KOC80, MOR80). In this paper we will present our studies of the light emission of SiF₄-O₂ plasmas. In these plasmas SiO₂ formation was shown to take place (BEE85, KUP78). To try to understand more of these discharges we analysed the variation in intensity of several bands and lines in the spectra as a function of the composition of the mixture SiF₄-O₂.

Experimental.

A schematic drawing of the experimental setup is given in figure 1. The gas discharge was generated in a quartz tube which diagonally crosses a waveguide at an angle of 30 degrees. Microwave power (2.45 GHz, 0-875 W) was generated with a magnetron (Toshiba 2M172). At the end of the waveguide a waterload absorbs the remaining power. In this configuration operating powers of the plasma up to 300 W could be achieved. The quartz tube can be evacuated down to 10⁻⁶ mbar with an oil diffusion pump. The operating pressure of the plasma (1-100 mbar) is maintained with a throttle valve in conjunction with the rotary pump (D 16BC Leybold Heraeus, filled with Pomblin). Two mass flow controllers (Inacom Instruments F-201MF) were used to regulate the gas flows (SiF₄: 0-200 mbarl/min, O₂: 0-500 mbarl/min). SiF₄ and O₂ were purchased from Matheson and Hoekloos respectively and used without further purification.

The emission spectra of the discharges were measured with two spectrometers. In the range of 200-500 nm a 25 cm Carl-Leiss monochromator was
used with a holographic grating (1200 lines/mm, blaze 250 nm) with a EMI 9789 QB photomultiplier. In the range of 360-850 nm a 50 cm Jena monochromator with flintglass prisma was used in conjunction with a EMI 9558 photomultiplier.

Results.

Emission spectra of pure O₂ and SiF₄ discharges were studied as well as those of several mixtures of SiF₄ and O₂. Spectra in the range of 200-450 nm are shown in figure 2a-c. In figure 2b the spectrum of the pure SiF₄ discharge is shown. In this spectrum most structures can be recognized and attributed to the SiF and SiF₂ radicals. The α, β, γ and η bands of SiF and the $\tilde{a}^3B_1 \rightarrow X^1A_1$ and $A^3B_1 \rightarrow X^1A_1$ bands of SiF₂ are clearly visible. Also a few Si lines can be seen.

In the O₂ spectrum (fig. 2c) only 0 lines and 2 unidentified band structures near 280 and 300 nm arise. The spectrum of the SiF₄-O₂ discharge as shown in fig. 2a is not a simple superposition of the pure SiF₄ and O₂ spectra. The most remarkable features are:

1. Upon the β and γ bands of SiF and the $\tilde{a}^3B_1 \rightarrow X^1A_1$ band of the SiF₂ a new and intense structure arises. This can be ascribed to the $1\Pi \rightarrow 3\Sigma^+$ transition in SiO.  
2. The intensity of the α band of SiF decreases by a factor of 5.  
3. Adjacent to the α band of SiF a structure that most likely can be attributed to SiO($^1\Sigma^- \rightarrow 3\Pi$ (TAL70) or $^3\Sigma^- \rightarrow a^3\Pi$ (SUC75)) increases in intensity by a factor of 10. The appearance of this band in the pure SiF₄ spectrum may be due to evaporation (etching) of SiO₂ or SiO from the tube-wall.  
4. The intensity of the $\tilde{a}^3B_1 \rightarrow X^1A_1$ band of SiF₂ is increased by a factor of 7.  
5. The most intense structure of the O₂ spectrum, the unidentified bands at 280-290 nm and 300-316 nm, have completely disappeared in the spectrum of the mixture.

The spectra at longer wavelengths (fig. 3a-b) show a strong presence of atomic lines and remarkably low emission from ionic species. This occurs as well in pure SiF₄ (fig. 3a) and O₂ as in the mixtures (fig. 3b). In the SiF₄ spectrum also a few molecular bands in the 500-575 nm region are visible. These have not been identified yet. A weak continuum from 450 to 725 nm also could not be ascribed to a known transition. The differences between the spectra of the pure compounds and the mixtures of SiF₄ and O₂ in the longer wavelength region are:

1. The F lines increase in intensity when O₂ is added.  
2. The O lines decrease in intensity when SiF₄ is added.  
3. The bands in the SiF₄ spectrum between 500 and 575 nm have completely disappeared in the mixtures.

For some structures in the spectra the dependence of their intensity on the composition of the mixtures is given in fig. 4.

Discussion.

From fig. 4 it becomes clear that addition of small quantities of SiF₄ to O₂ discharges and of O₂ to SiF₄ discharges has great influence on the intensities of several features in the emission spectrum of the plasma. The most remarkable changes occur when SiF₄ is added to an O₂ discharge. The disappearance of the O₂ bands near 300 nm and the strong rise of the SiO bands may be related. Since reaction of O₂ with SiF₄ and its
ground state radicals are thermodynamically unfavourable (BEE85) the reaction mechanisms to form SiO must involve excited species.

A possible source of these bands is the O2⁺ ion. The energy difference between the a⁴Π_u and X²Π_g states (4.0 eV) fits very well with the wavelength of the emitted light. The transition O₂⁺(a⁴Π_u) → O₂⁺(X²Π_g) is optically forbidden. This was confirmed in ICR experiments (SAE85) in which the lifetime was found to be in the order of at least a few ms. In view of the difference in multiplicity of this O₂⁺(a⁴Π_u) state and the O₂ ground state(X²Σ_g⁻) it is not surprising that radiationless decay via interaction with the latter is not a competitive process. Therefore the O₂⁺(a⁴Π_u) state is likely to decay to the O₂⁺ ground state emitting a photon in the 300 nm range. The high microwave power applied could cause a relatively high ionisation degree of the plasma that subsequently causes the excited ions to be produced. In other experiments (SAE85) we found the charge transfer

\[ \text{O}_2^+\text{(a}^4\Pi_{u}) + \text{SiF}_4 \rightarrow \text{SiF}_4^+ + \text{O}_2 \]

to be a very fast reaction. This explains why the emission disappears when only small quantities of SiF₄ are added to the O₂ discharge.

Although this model seems likely further research is necessary. In future experiments, among others mass spectrometry, we hope to find more evidence for the above mentioned processes.

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Fig. 1. Schematic drawing of the experimental set-up.

Fig. 4. Relative intensities of some structures in the emission spectra as a function of the composition of the SiF$_4$ - O$_2$ mixtures. (pressure 15 mbar, microwave power 300 W). Indicated are:
1. 316 nm band structure in O$_2$ spectrum  
2. 532.9 nm O - line  
3. 645.6 nm F - line  
4. (0,3) vibrational transition in the $A'_1$- $X'_1A_1$ band of SiF$_2$ (401.0 nm)  
5. (0,6) vibrational transition in the $A'_2$-$X'$- $X'_1$ band of SiO (282.0 nm)  
6. (4,4) vibrational transition in the $a$ band of SiF (453.2 nm)
fig. 2. Light emission spectra from SiF$_4$ and or O$_2$ discharges at 1 mbar, 300 W absorbed microwave power. The spectra were recorded with a 0.25 m monochromator with holographic grating (1200 l/mm, blaze 250 nm).
Fig. 3. Light emission spectra (850-450 nm) from SiF₄ (3a) and SiF₄-O₂ (3b) discharges at 1 mbar, 300 mbar absorbed microwave power. The spectra were recorded with a 0.50m monochromator with flintglas prism. Lines marked with one dot (.) are F atom lines; lines marked with two dots (:) are O atom lines and three dots (i) indicate Si atom lines.