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LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF SiF PRODUCED BY IR MULTIPLE-PHOTON DISSOCIATION OF SiF4

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SUMMARY

Excitation spectra and dispersed fluorescence were measured in the β -system (B² Σ -X² π) of the SiF radical produced by multiphoton dissociation (MPD) of SiF4 with a TEA CO2 laser. Within the limits of error no effect of the wavelength of the photolysis laser on the spectra was found. Formation and decay kinetics of SiF during and after IR laser excitation , as monitored by LIF, are also presented. The temporal behaviour of the SiF LIF signal was different for different wavelengths of the CO2 laser. For wavelengths close to the linear absorption band there was no induction period in the formation of SiF. The pressure dependence of the kinetics was different for the two CO2 laser branches.

INTRODUCTION

Essential for the development of modern microelectronics technology is the diagnostics of chemically active gaseous components interacting with matter in the presence of different types of radiation, electron or ion beams. In order to understand the complex physical and chemical processes involved in laser or plasma-induced deposition or etching, detailed information on the spatial distribution, velocity, and temperature of molecules, radicals, and other reactive intermediate species in the vicinity of the respective surface is required. Direct measurement of such quantities in real time may be carried out by using various optical techniques, such as absorption spectroscopy, CARS, multiple-photon excitation and ionization, etc. Laser-induced fluorescence (LIF) proves as an ideal method for the detection of chemically reactive species, as it provides a highly sensitive, selective, and nonintrusive probe of the gas-phase concentration of atoms, molecules, free radicals, and ions, combined with high resolution in space and time. Using LIF, the kinetic constants, transition strengths, radiative life-

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times and other process-dependent parameters can be determined. LIF has been successfully used for the investigation of a large variety of material processing problems: detection and determination of concentration profiles of CF and CF2 radicals in fluorocarbon etching of silicon (ref. 1); quantitative measurements of SiCl radicals in the discharge of chlorine-containing silane compounds (ref. 2); spectroscopy of SiCl2 radicals in conventional flow and in a supersonic jet after UV photolysis of dichloro- and trichlorophenylsilane (ref. 3); detection of SiH2 produced in IR photolysis of organosilanes (ref. 4); identification of SiF2 as final product of silicon etching by fluorine (ref. 5). So far, however, there seem to be no reports on sensitive LIF detection in the β -System of the SIF radical, one of the most important intermediate species in silicon, silicon dioxide and silicon nitride etching by fluorine-containing compounds.

In our report we present the results on LIF detection, spectroscopy, and monitoring of the formation and decay kinetics of SiF produced by IR MPD of SiF4.

EXPERIMENTAL

Fig. 1 gives a schematic representation of the experimental setup. In order to obtain a sufficient concentration of SiF radicals



Fig. 1. Experimental set-up

in our experiments, the well-known process of IR MPD of fluorosilane by CO_2 laser radiation (ref. 6) was used. The pure SiF₄ gas (contaminations were checked by mass-spectrometer measurements before and after the experiment) filled a stainless-steel cell at room temperature (pressure range 33,...266 Pa). For the photolysis a line-tunable TEA CO2 laser was used, which provided a 400 nspulse with a 4 μ s tail. A fluence of up to 100 J/cm² was obtained in the centre of the cell by focussing with a NaCl lens (f = 80 nm). The nitrogen-laser pumped dye laser (GR20, Carl Zeiss Jena) generated light pulses with Ø.3 mJ, 7 ns fwhm pulse duration and .7 cm^{-1} spectral width in the range around 437 nm for excitation of the α -system (A² Σ -X² π) of the SiF radical and after frequency doubling 40 μ J, 5.5 ns fwhm pulses in the 279...290 nm range for excitation of the β -system (B² Σ -X² π). The dye laser beam, collinear and counterpropagating to the CO₂ laser beam, probed the central part of the photolysis region. Fluorescence was observed perpendicular to the incident beam with a fused quartz lens focused onto the entrance slit of a monochromator (SPM2, Carl Zeiss Jena). It was detected by a photomultiplier (EMI 9558QB), the output of which was monitored with a boxcar averager (BCI 280) and then registered on an X-Y recorder. For calibration of the wavelength scale, LIF signals from resolved rotational lines of the OH radical around 282 nm were used. The error for an individual measurement of the SiF bandhead position was ± 20 pm (± 2.4 cm⁻¹). The sensitivity was better than 5x10⁹ photons/cm³ from the reaction zone.

Three types of regimes were used in the LIF measurements:

(i) fluorescence excitation spectra obtained by scanning the dye laser frequency for a fixed observation wavelength

(ii) dispersed fluorescence spectra measured by scanning the monochromator for a given excitation wavelength of the dye laser

(iii) time-resolved monitoring of the LIF signal by delaying the dye laser pulse continuously with respect to the CO₂ laser pulse (jitter 8.5 ns).

RESULTS AND DISCUSSION

Fluorescence excitation spectra

All detected LIF signals originated from the β -system of the SiF radical, while it was not possible to get a LIF signal from the α system in the wavelength region around 437 nm. Excitation spectra were measured in the 273...290 nm range. For the v" = 0 \rightarrow v' = 1 transition it is shown in Fig. 2. As the ground state $X^2\pi_{r}$



Fig. 2. Fluorescence excitation spectrum of SiF radical, β -system B² Σ , v'= 1 + X⁴ π , v" = Ø (λ_{obs} =296.5 nm)

is split due to spin-orbit coupling, the spectra exhibit two subbands, corresponding to the $X^2\pi_{1/2}$ and $X^2\pi_{3/2}$ states. Assignments of the band heads are based on a calculated LIF spectrum, using literature data (refs. 7-8) The resolution does not allow assignments beyond these band head features.

Dispersed fluorescence spectra

The dispersed fluorescence was measured in the 292...325 nm range for excitation of the $X^2\pi_{3/2}$, $v'' = \emptyset \rightarrow B^2\Sigma$, $v' = \emptyset$ transition at 289.4 nm (Fig. 3).



Fig. 3. Dispersed fluorescence spectra of the SIF radical, β -system $\lambda_{\bullet \times c}$ =289.4 nm (B² Σ , v' = Ø $\rightarrow X^2 \pi_{3/2}$, v" = Ø) The bandhead positions of the Δv = 1, 2 transitions are in good agreement with previously reported data (ref. 9). The spin-orbit splitting of these transitions is clearly resolved.

It was also found that probing at 289.4 nm resulted in the occurence of fluorescent lines at wavelengths shorter than the excitation wavelength. This indicates high rovibrational excitation of the SiF radicals, causing spectral overlapping of the rotational features of different absorption bands.

Time-resolved fluorescence

As was shown by the observed spontaneous fluorescence, there was multiphoton absorption in the 9 μ m branch (for smaller fluences see ref. 10) as well as in the 10 μ m branch. By scanning the CO₂ laser frequency from the 9R(50) to the 10P(8) line, the efficient formation of SiF radicals was observed not only with excitation in the traditional wavelength range at the maximum of the SiF4 linear absorption spectrum (9P branch), but also with excitation in the 10R branch (detuning from the linear absorption maximum of Si- F_4 by 40...50 cm⁻¹). When the CO₂ laser fluences exceeded 10 J/cm^2 , MPD at pressures \geq 100 Pa proceeded more effectively with excitation in the 10R branch than in the 9P branch. This fact can be completely explained by the self-sensibilisation phenomenon. Here, a small fraction of SiF4 molecules in high rotational states can absorb laser radiation in a wavelength region shifted to the "red" of the linear absorption maximum. Then these "hot" molecules excite "cold" molecules to higher levels with more appropriate absorption cross sections, resulting in dissociation of SiF4.

The time behaviour of the SiF LIF signal was quite different for different excitation wavelengths of the photolysis IR laser (Fig. 5). For the 9P(40) line (9.7308 µm), which is near the linear absorption bandhead (9.709 µm), there was no induction period in the rise of the LIF signal, as was the case for the 10R(40) line (10.1226 µm). The pressure dependence of the SiF LIF signal was also different for these two CO₂ laser lines (Fig. 6). For excitation with the 10R(40) line three regions with different slope can be distinguished (curve I). For the 9P(40) line the pressure dependence was more linear (curve II). We could detect no SiF with excitation in the $10 \ \mu m$ branch below a pressure of $100 \ Pa \ SiF_4$. These results can be well explained by self-sensibilisation.



Fig. 4. Time dependence of SiF radical on delay between and OO_2 and dye laser pulses for different SiF4 pressures

Adye=289.4 nm, λob=295.8 nm a - 10R(40) line of CO₂ laser b - 9P(40) line of CO₂ laser Fig. 5. Pressure dependence of SiF LIF signal for differrent excitation CO₂ laser lines. Time delay 3 μ s I - 10R(40)

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