

## Yellow emission bands produced during gold etching in O<sub>2</sub>-CF<sub>4</sub> rf glow-discharge plasmas: Evidence for gas-phase AuF

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Distinctive optical emission bands have been observed during the etching of gold films in O<sub>2</sub>-CF<sub>4</sub> and O<sub>2</sub>-SF<sub>6</sub> rf glow-discharge plasmas. We suggest that the emission originates from gas-phase AuF, although AuO and the molecular ions AuF<sup>+</sup> and AuO<sup>+</sup> cannot be definitively ruled out as the emitting species. No optical spectra have previously been reported for any of these species in the gas phase. Conditions for producing the emission bands are outlined, and a representative spectrum is provided. Band positions for the tentatively identified ( $v'=v'',v''$ ) and ( $v'=v''-1,v''$ ) progressions could be reproduced with a (0,0) band origin  $\nu_{00}=17\,757\text{ cm}^{-1}$ , vibration frequencies  $\omega'_e=529.5\text{ cm}^{-1}$  and  $\omega''_e=560\text{ cm}^{-1}$ , and vibrational anharmonicities  $\omega'_e x'_e=2.5\text{ cm}^{-1}$  and  $\omega''_e x''_e=1.0\text{ cm}^{-1}$ , where the vibrational energies relative to the  $v=0$  levels are given by  $G_0(v)=(\omega_e-\omega_e x_e)v-(\omega_e x_e)v^2$ . The band structure could be qualitatively accounted for by a  ${}^1\Pi-{}^1\Sigma$  band system with an assumed  $B'_e$  of  $0.24\text{ cm}^{-1}$ ,  $B'_e=B''_e+2.75\times 10^{-3}\text{ cm}^{-1}$ ,  $\alpha'_e=4.5\times 10^{-3}\text{ cm}^{-1}$ , and  $\alpha''_e=1.0\times 10^{-3}\text{ cm}^{-1}$ , where the rotation constants are given by  $B_v=B_e-\alpha_e(v+\frac{1}{2})$ .

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### I. INTRODUCTION

To date, there is very little information available on the properties of the diatomic gold compounds AuF, AuO, and their ions. Some spectroscopic properties of AuF and AuO molecules were recently predicted in a theoretical paper by Schwerdtfeger *et al.* [1], but experimental data remain scarce. This is due, in part, to the rather special conditions required for the production of these species in significant quantities. AuO, for example, has been produced in small amounts by photolysis of O<sub>2</sub>-doped rare-gas matrices containing condensed gold atoms [2]. AuF has proven to be even more elusive, although there is indirect evidence that it may be produced during the explosion of Au wires in a F<sub>2</sub> ambient [3]. Not surprisingly, perhaps, it has been found that glow discharges of the sort used by the microelectronics industry for thin-film deposition and etching may be excellent sources for metal-containing diatomic species of spectroscopic interest (see, for example, the work of Page, Gudeman, and Mitchell [4]). Rather by accident, this was found to be the case for the Au-containing species whose emission is described here.

In this brief paper, we report on the observation of yellow optical emission bands produced during the etching [5] of gold films in O<sub>2</sub>-CF<sub>4</sub> and O<sub>2</sub>-SF<sub>6</sub> rf glow-discharge plasmas. We suggest that the emission originates from gas-phase AuF, although AuO and the molecular ions AuF<sup>+</sup> and AuO<sup>+</sup> cannot be definitively ruled out as the emitting species. No optical spectra have previously been reported for any of these species in the gas phase. Conditions for generating the emission bands are outlined. A representative emission spectrum is provided, along with a preliminary spectral analysis. It is hoped that our observations will stimulate additional investigations of this intriguing emission, preferably at a level of detail

sufficient to produce precise molecular constants and a more definitive assignment of the emitting species.

### II. APPARATUS

Several plasma systems were utilized for this study. Each consisted of a 40-liter-stainless-steel chamber (with one or two 20-cm-diameter glass windows) fitted with two planar, 30-cm-diameter electrodes. The electrodes were made of graphite or aluminum, and were separated about 10 cm. The top electrode was perforated, and the bottom electrode was solid. Samples were placed on the bottom electrode. Either electrode could be powered by a Plasma-Therm rf generator at 13.56 MHz. In the "plasma etching" (PE) mode, the top electrode was powered, and the bottom (sample) electrode was grounded; in the "reactive ion etching" (RIE) mode, the sample electrode was powered and the top electrode was grounded. Applied power densities were typically around 0.4 to 0.7 W/cm<sup>2</sup>. A variety of O<sub>2</sub>-CF<sub>4</sub> and O<sub>2</sub>-SF<sub>6</sub> gas mixtures were employed, typically at pressures in the range 40–650 mTorr, and at total flows of 50 to 400 SCCM (where SCCM denotes cubic centimeter per minute at STP).

The gold films used for the etching were typically 0.5- to 1.0- $\mu\text{m}$  thick (prior to etching), and were typically deposited on 57-mm-diameter silicon wafer substrates by electron beam evaporation.

Emission spectra were obtained with an optical multichannel analyzer (1451 Plasma Monitor with 1454 detector, EG&G/Princeton Applied Research). Light was collected through a sapphire window by an optical fiber, and dispersed with a 0.27-m monochromator (Jarrell-Ash Monospec 27). A 1200-groove/mm grating was typically used, giving a resolution of about 2 to 3 Å.

### III. OBSERVATIONS AND PROCEDURES

The yellow emission, when present, was clearly evident by eye, and appeared as a  $\sim 5$ -cm-diameter cloud suspended above the Au-coated wafer being etched. The emission (or "yellow glow") was observed during the etching of gold films in both  $O_2$ - $CF_4$  and  $O_2$ - $SF_6$  mixtures, and disappeared when the gold was consumed. A spectrum of this emission (observed in an  $O_2$ - $CF_4$  plasma) is shown in Fig. 1 (solid line). Two distinct band groupings are observed, a stronger one at 563–570 nm, and a weaker one at 581–589 nm. Some bands are narrow, and some are red degraded. The background spectrum (dotted line) was taken at a later time, when the yellow emission was very nearly gone. The violet-degraded emission at 561 nm (present in both traces) is a strong CO band, the Ångström system  $B^1\Sigma(v'=0) \rightarrow A^1\Pi(v''=3)$  transition [6].

It should be noted that the wavelength scale in Fig. 1 is based on a linear extrapolation between the positions of the 563- and 581-nm bands, whose wavelengths were determined by comparison to the position of known-wavelength Ar lines present in the same spectral region when 2% Ar was added to the discharge.

A variety of plasma conditions were examined in efforts to maximize the intensity and/or duration of the yellow glow. Yellow glows were observed in both the "plasma etching" and "reactive ion etching" modes. No yellow glow was seen in pure  $O_2$  or  $CF_4$  plasmas, and the best results were obtained for  $CF_4$  concentrations in the range of 15–50%. The yellow emission would usually peak several minutes after the plasma was turned on, suggesting that the sample needed to be heated or "conditioned" before any Au-containing species could be volati-

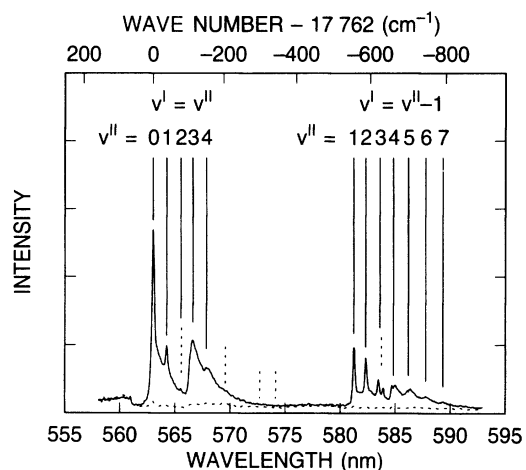


FIG. 1. The spectrum of the yellow emission produced during gold etching in an  $O_2$ - $CF_4$  rf glow-discharge plasma (solid line); a background emission trace ( $\times 2$ ) taken at a later time, when the yellow emission is very nearly gone. The dotted vertical lines correspond to the positions of atomic Au or  $Au^+$  lines. The wavelengths and energies of the emitting level for these lines are as follows [8]: 565.57 nm ( $Au I$ , 8.51 eV), 569.57 nm ( $Au II$ , 10.62 eV), 572.68 nm ( $Au I$ , 8.75 eV), 574.12 nm ( $Au I$ , 9.75 eV), and 583.73 nm ( $Au I$ , 6.75 eV).

lized in appreciable amounts. Gold films of  $\sim 0.7\mu m$  in thickness would typically be consumed after providing a yellow glow for about 20–25 min, implying an etch rate of order 300 Å/min. The intensity of the yellow emission was estimated by comparing it to that of the three O atom lines at 777.2–777.5 nm, which produced the strongest feature in the emission spectrum. Under representative conditions (20%  $CF_4$ , 500 mTorr, and 0.7 W/cm<sup>2</sup>), the yellow bands had a steady-state relative intensity of about 20% (based on the ratio of the integrated "signal minus baseline" intensities in the regions 562–573 nm and 776–778.1 nm). If the *peak* (rather than *integrated*) signals were to be compared, the relative intensity of the strongest yellow band would be about 7% for measurements with the same  $\sim 2$ - to 3-Å resolution as utilized in Fig. 1.

Rotational temperatures ( $T_{rot}$ ) in the discharge were estimated from the shape of the  $O_2 b^1\Sigma_g^+(v'=0) - X^3\Sigma_g^-(v''=0)$  emission band at  $\sim 760$  nm [7]. In pure- $O_2$  discharges at 500 mTorr, we found  $T_{rot} = 400 \pm 30$  K at 0.21 W/cm<sup>2</sup> and  $T_{rot} = 580 \pm 40$  K at 0.42 W/cm<sup>2</sup>, from which we estimate a  $T_{rot}$  of 550–750 K for the 0.4- to 0.7-W/cm<sup>2</sup> power range used in the experiments.

### IV. DISCUSSION AND ANALYSIS

Based on the following, we believe that the emitting species is likely to be  $AuF$  or a diatomic Au-containing ion such as  $AuF^+$  or  $AuO^+$ .

(1) The yellow emission bands were never observed in the absence of a gold sample, and always disappeared when the gold film was consumed, suggesting that the emitting species contains Au.

(2) A yellow emission (with a spectrum identical to that shown in Fig. 1, except for the CO peak) was also observed during gold etching in an  $O_2$ - $SF_6$  plasma with Al electrodes, implying that the emitting species does not contain carbon.

(3) The well-resolved band structure of the emission suggests that the emitting species is a diatomic molecule. Polyatomic species would be expected to have much broader spectra, and none of the spectrum can be accounted for by the atomic emission lines [8] of O or F. The possibility that a few of the narrow emission bands might originate from atomic gold species was carefully considered, since five emission lines [8] of Au or  $Au^+$  fall in this region of the spectrum. The positions of these lines are marked in Fig. 1; the emission wavelengths and energies of the emitting levels are listed in the figure caption. While there may be some coincidences between the atomic line positions and features in the observed spectrum, it is clear that the bulk of the emission is not due to atomic species.

(4) The possibility that the yellow glow might have arisen from a silicon-containing species originating from a reaction with the substrate was eliminated by the fact that the observed emission bands did not match any of those reported for  $Si_2$ ,  $SiO$ ,  $SiO_2$ ,  $SiO^+$ ,  $SiF$ ,  $SiF_2$  and  $SiF_3$  (in Ref. [6]), or for  $AuSi$  (in Ref. [9]).

(5) The above considerations suggest that the emitting

species is a diatomic molecule or ion containing either two Au atoms, or one Au atom in combination with F or O, i.e., Au<sub>2</sub>, AuF, or AuO or their ions [10]. The estimated vibration frequencies of the emitting species ( $\omega_e \sim 560$  and  $530 \text{ cm}^{-1}$ , see below) allow us to eliminate Au<sub>2</sub><sup>+</sup> (which has a calculated [1] ground state  $\omega_e \approx 110 \text{ cm}^{-1}$ ). For the same reason, Au<sub>2</sub> is also unlikely to be the emitting species [the known  $\omega_e$  are all between  $\omega_e(a) \approx 88 \text{ cm}^{-1}$  and  $\omega_e(X) \approx 190 \text{ cm}^{-1}$  [11]]. In addition, the only yellow bands of Au<sub>2</sub> (belonging to the  $a^3\Sigma_{1u}^+ - X^1\Sigma_g^+$  system [11]) include prominent features in the 567–581-nm region not present in Fig. 1. AuO cannot be ruled out as the emitting species on the basis of its vibration frequency (measured [2] to be  $\sim 600 \text{ cm}^{-1}$  for the ground state), but is tentatively [12] ruled out on the grounds that its only observed emission bands [2] (produced by Xe-lamp irradiation of matrix isolated molecules) were found in the blue-violet (i.e., 417–455 nm), with little shifting expected for the gas-phase spectra. This leaves only AuF and the ions of AuF and AuO as the probable emitting species.

While either AuF or the molecular ions AuF<sup>+</sup> or AuO<sup>+</sup> may be the emitting species, we are inclined to favor AuF due to its expected abundance relative to AuF<sup>+</sup> or AuO<sup>+</sup>.

The formation of gas-phase AuF by some reaction of a volatile, gold-contained etch product with oxygen may explain why no yellow emission could be observed during gold etching [5] in pure CF<sub>4</sub> plasmas. One such reaction is



O atoms are known to be present in oxygen-containing plasmas, and AuF<sub>3</sub> is known to be relatively volatile [13]. The volatility of AuF<sub>3</sub> may, in fact, account for why gold films can be etched in O<sub>2</sub>-CF<sub>4</sub> and O<sub>2</sub>-SF<sub>6</sub> plasmas. Recent calculations [1] lead us to believe that reaction 1 is exothermic. We estimate a  $\Delta H$  for the reaction of  $-28 \pm 40 \text{ kJ/mol}$ , based on the enthalpies of formation  $\Delta H_f$  (at 298 K) of  $-364 \text{ kJ/mol}$  for AuF<sub>3</sub> (Ref. [14]),  $+249 \text{ kJ/mol}$  for O (Ref. [14]),  $-22 \text{ kJ/mol}$  for F<sub>2</sub>O (Ref. [14]), and  $-121 \pm 40 \text{ kJ/mol}$  for AuF (based on a calculated [1] dissociation energy of  $200 \pm 40 \text{ kJ/mol}$  and a measured [14]  $\Delta H_f$  of  $+79 \text{ kJ/mol}$  for F).

If AuF is indeed the emitting species, one might expect the spectrum of Fig. 1 to result from  $^1\Sigma - ^1\Sigma$ ,  $^1\Pi - ^1\Sigma$ , or  $^1\Pi - ^1\Pi$  transitions, since  $^1\Sigma$  and  $^1\Pi$  are the known electronic states for the homologous molecule CuF [15]. In addition, one would expect all of the peaks to be from a single isotope of AuF, since Au and F occur naturally in only one isotopic form. If it is assumed that the strongest band in the spectrum (at 563.0 nm) corresponds to the  $v'=0 \rightarrow v''=0$  transition, the (0,0) band origin  $\nu_{00}$  would be approximately  $17762 \text{ cm}^{-1}$ . It is not clear whether the observed transition is between two excited electronic states, or between an excited electronic state and the ground state. It seems likely that the 563–570- and 581–589-nm groupings are  $(v'=v'', v'')$  and  $(v'=v''-1, v'')$  progressions with the numbering shown in Fig. 1. This implies that  $\omega_e'' \approx 556 \text{ cm}^{-1}$ , and that

$\omega_e' \approx 525 \text{ cm}^{-1}$ . Calculated [1] values of the ground-state vibration frequency  $\omega_e(X)$  for AuF are similar to these values, about  $500 \text{ cm}^{-1}$ .

It was found that the observed band structure could be qualitatively accounted for by emission from a molecule with the  $B$  values, electronic states, and rotational temperature expected for AuF. Figure 2 shows a simulated spectrum for 15 bands of a  $^1\Pi - ^1\Sigma$  band system. The simulation used the line strengths of Ref. [16], the band intensities of Table I, Gaussian smoothing with a full width at half maximum of  $3 \text{ \AA}$ , and a  $T_{\text{rot}}$  of 550 K. The molecular constants used for this spectrum were  $\nu_{00} = 17757 \text{ cm}^{-1}$ ,  $\omega_e' = 529.5 \text{ cm}^{-1}$ ,  $\omega_e'' = 560 \text{ cm}^{-1}$ ,  $\omega_e'x_e' = 2.5 \text{ cm}^{-1}$ , and  $\omega_e''x_e'' = 1.0 \text{ cm}^{-1}$ , where the vibrational energies relative to the  $v=0$  levels are given by  $G_0(v) = (\omega_e - \omega_e x_e)v - (\omega_e x_e)v^2$ . The rotational constants were assumed to be of the form  $B_v = B_e - \alpha_e(v + \frac{1}{2})$ .  $B_e''$  was taken to be  $0.24 \text{ cm}^{-1}$  (computed from the  $2.0\text{-\AA}$  value of  $r_e$  calculated [1] for the  $X^1\Sigma_g^+$  state of AuF). The constants  $B_e' = B_e'' + 2.75 \times 10^{-3} \text{ cm}^{-1}$ ,  $\alpha_e' = 4.5 \times 10^{-3} \text{ cm}^{-1}$ ,  $\alpha_e'' = 1.0 \times 10^{-3} \text{ cm}^{-1}$ , and the  $\omega_e x_e$  values were determined empirically. The centrifugal distortion constants (estimated as  $D_e = 4B_e^3/\omega_e^2$  [16]) were omitted from the analysis, since they had a negligible effect on the band shapes. The similarity of the calculated and observed spectra conclusively indicates that the emission is from a diatomic molecule. In addition, it lends weight to the case that AuF is the emitting species, since a somewhat different band structure would be expected for transitions between the  $^2\Pi$  and  $^2\Sigma$  states of AuO (and the isoelectronic AuF<sup>+</sup>).

An even closer match to the observed spectrum was found if  $T_{\text{rot}}$  was assumed to be 300 K for  $v'=0$  and 1, and 1200 K for  $v' \geq 2$ . Such a variation in  $T_{\text{rot}}$  might occur if the nascent AuF internal state distribution is nonstatistical and the AuF product molecules are too short lived to completely thermalize.

Error limits can be estimated from the sensitivity of

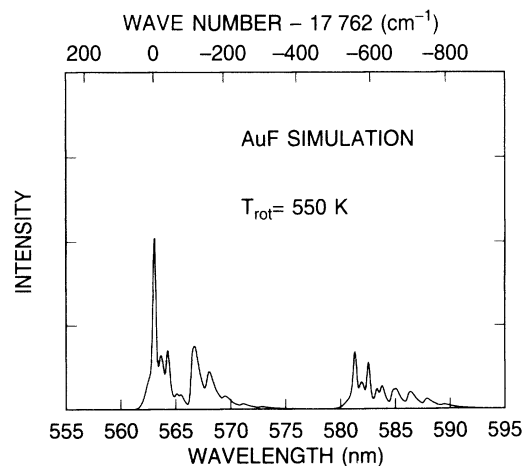


FIG. 2. A simulated spectrum for the possible  $^1\Pi - ^1\Sigma$  band system of AuF. The molecular constants are described in the text, and the band intensity factors are given in Table I.

TABLE I. Band intensity factors used to generate the spectrum of Fig. 2.

$v''$	0	1	2	3	4	5	6	7
$v'=v''$	1.00	0.39	0.11	0.63	0.30	0.08	0.04	0.02
$v'=v''-1$		0.38	0.29	0.19	0.19	0.16	0.09	0.03

the simulated spectrum to small changes in the values of the molecular constants. While the band shapes are very sensitive to the values of  $B_{v'} - B_{v''}$ , they are quite insensitive to the absolute values of the  $B_v$ . With only a moderate adjustment in  $T_{rot}$ , equally good fits could be obtained with a  $\pm 30\%$  change in the assumed  $B_e''$  value, providing the  $\Delta B_e \equiv B_e' - B_e''$  and  $\alpha_e$  values remained unchanged. Verification of the assumed  $B_e''$  value will require rotationally resolved data. Roughly similar band shapes (or, equivalently, roughly similar values of  $B_{v'} - B_{v''}$ ) could be generated for  $\alpha_e''$  and  $\Delta B_e$  values within 50% of those used in the simulation, and for  $\alpha_e'$  values within 30% of those used. Somewhat better relative accuracies are expected for the  $\omega_e x_e$  values, and the  $\omega_e$  values should be good to  $\sim \pm 2 \text{ cm}^{-1}$ . Where possible, the choice of constants within these ranges was guided by the relationships between  $B_e$ ,  $\alpha_e$ ,  $\omega_e$ , and  $\omega_e x_e$  expected for a Morse oscillator [16]. However, these relationships were found to hold poorly, especially for the upper state. For example, the values of  $\alpha_e$  calculated from  $\alpha_e = 6(\omega_e x_e B_e^3)^{1/2} / \omega_e - 6B_e^2 / \omega_e$  were two to three times smaller than the  $\alpha_e$  values required to fit the spectrum, suggesting that the AuF potential-energy curves are not well described by a Morse potential.

## V. SUMMARY

The distinctive yellow optical emission bands observed during the etching of gold films in  $\text{O}_2\text{-CF}_4$  and  $\text{O}_2\text{-SF}_6$  rf glow-discharge plasmas were tentatively attributed to emission from gas-phase AuF, although AuO and the molecular ions  $\text{AuF}^+$  and  $\text{AuO}^+$  could not be definitely ruled out. Conditions for producing these emission bands were outlined. It was found that the observed spectrum could be qualitatively accounted for by a  ${}^1\Pi\text{-}{}^1\Sigma$  band system with a (0,0) band origin  $\nu_{00} = 17\,757 \text{ cm}^{-1}$ , vibration frequencies  $\omega_e' = 529.5 \text{ cm}^{-1}$  and  $\omega_e'' = 560 \text{ cm}^{-1}$ , vibrational anharmonicities  $\omega_e' x_e' = 2.5 \text{ cm}^{-1}$  and  $\omega_e'' x_e'' = 1.0 \text{ cm}^{-1}$ , an assumed  $B_e''$  of  $0.24 \text{ cm}^{-1}$ ,  $B_e' - B_e'' = 2.75 \times 10^{-1} \text{ cm}^{-1}$ ,  $\alpha_e' = 4.5 \times 10^{-3} \text{ cm}^{-1}$ , and  $\alpha_e'' = 1.0 \times 10^{-3} \text{ cm}^{-1}$ .

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- the possibility that gold was not contained in the emitting species but rather was a catalyst required for its formation.  $\text{O}_2$ ,  $\text{O}_2^+$ ,  $\text{F}_2$ , and  $\text{F}_2^+$  were eliminated from further consideration since none of the yellow emission bands reported in Ref. [6] for these species could account for the spectrum in Fig. 1. FO and  $\text{FO}^+$  were eliminated on the basis of their ground-state  $\omega_e$  values [J. M. Dyke, N. Jonathan, J. D. Mills, and A. Morris, *Mol. Phys.* **40**, 1177 (1980)], which are at least a factor of 2 larger than the  $\omega_e \sim 556 \text{ cm}^{-1}$  value estimated for the emitting species.
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