Infrared Chemiluminescence from XeF_2-Silicon-Surface Reactions

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Infrared luminescence has been observed and the emission spectra in the 2.5–8.0-μm region determined for a silicon crystal exposed to XeF_2 gas. In contrast to the broad and structureless emission in the uv and visible regions previously reported for some gas-solid systems, the ir spectrum exhibits characteristic fine structure. Furthermore, the emitted radiation shows strong polarization and angular dependence indicating that the emitting species are on the crystal surface.

Chemiluminescence in the ultraviolet and visible region of the spectrum has been observed for a number of gas-solid systems, e.g., O_2, NO, and CO on W,[1] O_2 on Si,[2] O_2 on Al and Mg,[3] halogens on Na,[4] O_3, NO_2, etc., on Ba and Mg,[5] F_2 on Al, Ti, and Si,[6] and CF_4-O_2 plasma etching of Si.[7] Generally, the emission is weak and the spectra are broad and structureless.[3-7] They are difficult to interpret and little is known about the origin of the light emission process which occurs during the surface reaction. Infrared luminescence from gas-phase chemical reactions is a well-known phenomenon and has been successfully employed to investigate reaction dynamics.[8] In an exothermic surface reaction, it is quite possible that the reaction products can also be formed in excited vibrational states. In certain systems with sufficiently short radiative lifetimes it will be possible to dissipate the excess energy by photon emission. The emitted radiation is expected to contain chemical information about the identity of the excited surface species. In this paper, I report the first observation of ir chemiluminescence from the reaction of silicon with XeF_2 gas. Silicon was chosen for the initial study because the reaction

$$2XeF_2(\text{gas}) + Si(\text{solid}) \rightarrow SiF_4(\text{gas})$$

has been shown to occur very rapidly at room temperature.[9] Etch rates as large as 7000 Å/min were measured when the XeF_2 pressure was less than 1.4×10^{-2} Torr, and the rate varied linearly with the pressure of XeF_2. I have independently confirmed this rapid reaction rate. The most important products of the reaction were gaseous Xe and SiF_4 as determined from mass-spectrometric analysis.

The experimental apparatus in the present experiments consists of a diffusion pumped vacuum chamber (base pressure $\sim1\times10^{-7}$ Torr) with a sputter ion gun for crystal surface cleaning and BaF_2 and saphire optical view ports. A photomultiplier, a photon-pulse counter, and the saphire window were used for detecting chemiluminescence in the uv, visible, and near ir. Details of these experiments will be published elsewhere. For ir measurements, a BaF_2 window, an ir grid polarizer, a Ge lens, a circular-variable-filter monochromator (CVF), and a liquid-nitrogen-cooled Ge:Au detector were used. The signal is modulated with a chopper and detected with a lockin amplifier. The silicon single-crystal wafer (n type, 1.0 Ω cm, 1 in. diam) is held with an aluminum ring and a thin stainless steel backing plate. The sample holder is attached to a rotary feedthrough for variation of the polar angle (θ) between the surface normal and the direction of detection, which is fixed in the laboratory. The polarizer can be rotated with respect to the plane formed by these two axes, namely, the P and S polarizations parallel and perpendicular to this plane, respectively. The CVF monochromator (from Optical Coating Lab, Inc., Santa Rosa, California) driven by a motor consists of three segments covering the spectral range from 2.5 to 14.5 μm. The wavelength varies linearly with the angle of rotation and is calibrated with the absorption spectra of some known gases. The main spectral region of interest reported here is limited to <8.0 μm by the sensitivity of the Ge:Au detector. With the optical arrangement and the slit (3.2 mm) used for the experiments, the spectral resolution is about 65 cm^{-1} at 7.0 μm.

XeF_2 is a solid with a vapor pressure at room temperature of about 4.5 Torr.[10] The vapor is introduced into the vacuum chamber by opening a leak valve which isolates the solid XeF_2 from the vacuum. The experimental procedure involves cleaning the air-exposed silicon by Ar^+-ion bombardment to remove surface oxide which does not react with XeF_2.[9] The sample is then exposed to XeF_2. The gate valve separating the reaction chamber and the vacuum pumping system is opened and the leak valve controlling the XeF_2

flow is adjusted so that a steady-state reaction with a gas pressure of 1.5×10^{-2} Torr is maintained. This gas consists mainly of XeF_2 and the Xe and SiF_4 reaction products. The ir spectrum with either P or S polarization is obtained by scanning the CVG, as a function of crystal angle θ.

Figure 1(a) shows the typical ir luminescence spectrum at $\theta=0°$, i.e., the surface normal coincides with the axis of detection. The spectra are identical for both P and S polarizations, with structures between 4 and 8 μm clearly evident. As θ increases, the spectrum with P polarization is separated from the spectrum with S polarization, with the former always stronger in emission intensity. The spectra with the P and S polarization components at θ near 55° are shown in Fig. 1(b). Near grazing incidence, $\theta\simeq 90°$, the emission intensity decreases by more than a factor of 10, as compared with that at $\theta=55°$. Apart from the emission intensity, the basic spectral features remain unchanged as a function of θ. Also indicated in Fig. 1 are the spectral range of the three CVF segments. Double bars in the figure show the junction of two successive segments. The peak intensities for the emission bands at 7.71, 5.63, and 4.15 μm are shown as a function of θ in Fig. 2. The characteristics of the bands at 6.98 and 5.63 μm are similar to those of the 7.71-μm band with the P component increasing in intensity with θ, peaking at $\theta\simeq 55°$, and decreasing as θ becomes larger. On the other hand, the S component decreases monotonically with the variation of the crystal angle.

To interpret the experimental results, I have obtained the gas-phase absorption spectra of SiF_4 using the same experimental apparatus. Below 8 μm, there are three major bands due to the $2\nu_3$, $\nu_1+\nu_3$, and $\nu_2+\nu_3$ transitions at 4.90, 5.53, and 7.80 μm, in good agreement with the previous measurement.[11] The observed emission bands at 7.71 μm, 5.63 μm, and a shoulder near 4.90 μm are reasonably close to the SiF_4 which is the final product of the XeF_2-Si reaction. The assignment for the emission band at 6.98 μm is not clear. Bailey, Hale, and Thompson[11] reported a very weak band at 6.91 μm due to the $\nu_3+\nu_4$ transition of SiF_4. If the observed emission band were due to this transition, then some of the vibrational modes of SiF_4 would be quite preferentially populated. It is more likely, however, that the 6.98-μm band may be due to a different chemical source. The foregoing assignment of the emission bands should be considered only tentative pending on further investigation. Nevertheless, it is important to point out that strong evidence exists to suggest that the emitted radiation may have a "molecular" origin.

It should also be noted that the general spectral contour shown in Fig. 1 is quite different from that of a gas-phase spectrum, namely, there is a broad background under the resolved peaks. Because the XeF_2-Si reaction is exothermic, it is expected that the Si surface temperature would

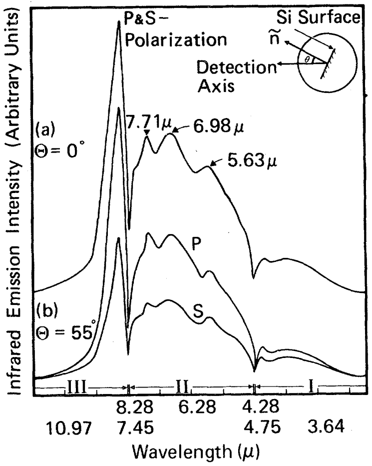

FIG. 1. The ir emission spectra for the XeF_2-Si system at (a) $\theta=0°$ and (b) $\theta=55°$; θ is defined as the angle between the surface normal ($\tilde{n}$) and the detection axis. Double bars indicate the junctions of the three CVF segments.

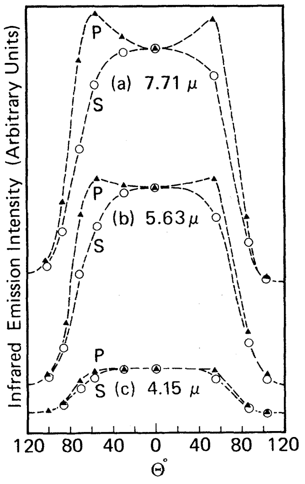

FIG. 2. The ir emission intensity with P and S polarization vs θ for the emission bands at (a) 7.71 μm, (b) 5.63 μm, and (c) 4.15 μm.

rise above the ambient temperature and the crystal would emit thermal radiation. I have measured the substrate temperature with an iron-constantan thermocouple attached to the crystal surface in reaction with XeF_2. A temperature of 52°C, i.e., about 30°C above the room temperature, is obtained. The ir emission spectrum for a silicon crystal at about 50°C in the vacuum chamber was subsequently measured. The spectrum exhibits a similar contour with some broader features, but it is less intense and does not show the strong peaks such as those at 7.71, 6.98, and 5.63 μm observed for the XeF_2-Si system. The presence of 1.5×10^{-2} Torr of SiF_4 gas in equilibrium with a Si crystal at 50°C does not significantly alter the emission spectrum. Furthermore, in the absence of XeF_2, the emitted radiation of the Si substrate is unpolarized at any given angle θ (further discussed below). I, therefore, conclude that the ir luminescence for the XeF_2-Si system is partially due to the thermal emission of the Si crystal at 50°C, and partially from the photon emission of the excited surface species. Gaseous SiF_4 in thermal equilibrium with the substrate does not make a significant contribution to the observed emission.

The observed polarization and angular dependence shown in Figs. 1 and 2 further supports the conclusions drawn above. Greenler[12] recently showed that light emitted from molecules adsorbed on a metal surface should exhibit a strong angular dependence due to interference of the direct and the reflected wave of the emitted radiation. Accordingly, the emission for a dipole oriented parallel to the surface normal of a metal can have an intensity maximum in the 70°–80° region and the maximum can be about two orders of magnitude larger than the emission due to dipoles oriented perpendicular to the surface normal. I have performed a similar calculation for an emitting dipole adsorbed on a silicon crystal which is quite transparent between 2 and 12 μm. In this spectral region, the emission from a dipole oreinted parallel to the surface normal (P polarization) has an intensity peak at $\theta \simeq 60°$ and the maximum intensity is about a factor of 10 larger than for the other two orthogonal orientations. If the emitting dipole is randomly oriented on a silicon surface, the emission at $\theta = 0°$ is nonzero and both the P and the S components have the same intensity. When θ increases, the P component has a peak at $\theta \simeq 60°$, but the S component decreases monotonically. At $\theta = 90°$, both components disappear. This calculated angular dependence agrees reasonably well with that observed in the XeF_2-Si system (Fig. 2), except that at $\theta = 0°$, the observed emission intensity is substantially higher than the calculated value. This is probably due to the contribution from the unpolarized thermal emission of the Si substrate. The thermal radiation decreases slowly as a function of θ because of the optical detection geometry. The emitted radiation is not likely originated from excited gas-phase species which should have a sifficiently long lifetime to form an emission region a few millimeters or greater from the surface. If this were the case, I should have observed a sufficiently high emission intensity at $\theta = 90°$, and the emission would be unpolarized. The qualitative agreement between the observed polarization and angular dependence and the calculations based on the dipole emission model strongly suggests that the photon-emitting excited species are on the silicon surface. Until now, such polarization and angular behavior has not been experimentally demonstrated in a system supposedly exhibiting surface chemiluminescence.

Based on the experiments reported in this paper, I have reason to believe that infrared chemiluminescence can be developed into a very useful method for studying exothermic gas-solid interactions and, in particular, for the identification of reaction intermediates and for the determination of surface chemical kinetics.

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[1] B. McCarrol, J. Chem. Phys. 50, 4758 (1969).

[2] L. E. Brus and J. Comas, J. Chem. Phys. 54, 2771 (1971).

[3] B. Kasemo, Phys. Rev. Lett. 32, 1114 (1974).

[4] B. Kasemo and L. Wallden, Surf. Sci. 53, 393 (1975).

[5] P. I. Cohen, S. Abramowitz, and H. P. Broida, Surf. Sci. 69, 601 (1977).

[6] T. J. Chuang, unpublished.

[7] Y. Horrike and M. Shibagaki, *Extended Abstracts, Proceedings of the 151st Electrochemical Society Meeting* (Electrochemical Society, Inc., Princeton, N. J., 1977), Vol. 77-1, p. 619.

[8] J. K. Cashion and J. C. Polanyi, Proc. Roy. Soc. London, Ser. A 258, 529 (1960).

[9] H. F. Winters and J. W. Coburn, Appl. Phys. Lett. 34, 70 (1979).

[10] J. H. Holloway, *Noble-Gas Chemistry* (Methuen, London, 1968), p. 108.

[11] C. R. Bailey, J. B. Hale, and J. W. Thompson, Proc. Roy. Soc. London 167, 555 (1938).

[12] R. G. Greenler, Surf. Sci. 69, 647 (1977).