Origin of porous silicon photoluminescence: Evidence for a surface bound oxyhydride-like emitter

James L. Gole, Frank P. Dudel, and David Grantier School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332

David A. Dixon

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, K1-83, Richland, Washington 99352

(Received 14 February 1997)

Time-dependent excitation spectroscopy coupled with quantum chemical calculations is used to demonstrate that the photoluminescence (PL) resulting from the ultraviolet optical pumping of an etched porous silicon (PS) surface results from a silicon oxyhydride-like fluorophor bound to the PS surface. The time-dependent PL, in both aqueous (HF/H₂O and HF/CH₃OH/H₂O) and nonaqueous [MeCN/HF (anhydrous)] etching media, has been monitored both in situ, during the etching cycle and before the PS sample is removed from the etching solution, and ex situ, after removal of the PS sample from the etching solution. The early appearance in time of the PS luminescence is consistent with the formation of a surface bound emitter created on a time scale $(\leq 10 \text{ s})$ much shorter than that needed for pore formation. Laser excitation spectra (PLE) over the wavelength range extending from 193 to 400 nm produce an almost identical time-dependent PL emission feature between 550 and 700 nm. Influenced strongly by the chemical composition of the etch solution, an intermediate "green" emitter can be excited with select laser pumping wavelengths and observed to transform to the final "orange-red" luminescent product. In conjunction with experiments whose focus has been to compare the time-dependent PL after ArF (193 nm) and N_2 (337 nm) laser excitation (PLE), the data suggest the pumping of an excited-state manifold for a molecule-like species followed by rapid relaxation via nonradiative transitions down the manifold and the subsequent emission of radiation at much longer wavelength. Detailed quantum chemical modeling supports this interpretation and suggests a correlation to changes in the bonding associated with electronic transitions that involve silanone-like ground electronic singlet states and their lowlying triplet excitons. Especially important are those changes involving SiO related bonds. A substantial shift in the excited-state manifold, relative to the ground state, correlates with the character of the observed PL spectra as the excitation to a manifold of states greatly shifted from the ground electronic state produces a considerable redshift of the PL spectrum ($\sim 600-800$ nm) compared to the known peak wavelength of the PLE (excitation) spectrum at 350 nm. The combination of quantum chemical modeling and time-dependent spectroscopic studies also suggests that the multiexponential PL decay commonly observed as a function of increasing wavelength (550-750 nm) after excitation at 355 nm results primarily from nonradiative cascade. The optical detection of magnetic resonance (ODMR) spectrum obtained for PS and associated with a triplet exciton is assigned to an oxyhydride-like emitter possessing silicon-oxygen and silicon-hydroxide fluorophors similar to the much more complex annealed siloxene. Calculated infrared spectra are correlated with experimentally observed features and are consistent with a surface-based oxyhydride-like emitting fluorophor. A recent analysis that associates the linewidth of the triplet ODMR spectrum with an inhomogeneous distribution of quantum confined crystallites is shown to be in error. We demonstrate that the correct extension of the arguments used in this analysis provides clear evidence for the existence of a common radiative center associated with a molecule-like species bound to the surface of the PS framework. The results obtained in this study are thus not consistent with quantum confinement and suggest a surface bound emitter as the source of the PS photoluminescence. [S0163-1829(97)01728-1]

I. INTRODUCTION

The discovery of room-temperature visible luminescence¹ from high surface area porous silicon (PS) structures formed in wafer scale, through electrochemical etching, has attracted considerable interest primarily because of its potential use in the development of silicon-based optoelectronics, displays, and sensors. The luminescence from porous silicon is thought to occur at or near the silicon surface. The efficiency and wavelength range of the emitted light are strongly affected by the physical and electronic structure of the surface

and, for *in situ* observations, by the nature of the etching solution.^{2,3} However, the source of the PS luminescence is controversial.

The most popular hypothesis invoked to explain the visible emission from PS asserts that the luminescence results from the radiative recombination of quantum-confined electrons and holes in columnar structures or undulating wires^{4–6} associated with the creation of pores and subsequently silicon nanoparticles. A blueshifting with increasing pore widening treatments^{1,7} has been interpreted as producing wire sizes well within the confinement limit. However, more re-

<u>56</u>

2137

cent experiments⁸ demonstrate the observation of *in situ* photoluminescence (PL) from both aqueous and nonaqueous etched samples prior to the formation of any pores. These experiments indicate that much less than 100 nm of silicon need be removed before the luminescence centers are formed. The topographical changes in the surface are consistent with the formation of emitting, constrained, surface species (oxyhydrides). A second explanation suggests the importance of the surface localized states created by irregularly shaped small crystallites which are not perfectly passivated and into which elementary excitations can be trapped prior to a recombination^{9,10} as bound states recombine radiatively.

Finally, a third hypothesis attributes the PS luminescence to surface-confined molecular emitters¹¹ including a molecular complex of silicon, oxygen, and hydrogen known as siloxene (Si₆O₃H₆). Stutzmann and co-workers^{12–14} have used the optical detection of magnetic resonance (ODMR) to establish that the "red" emission from PS results from a triplet exciton. Identifying the close analogy of both the ODMR, photoluminescence excitation (PLE), and photoluminescence spectra of PS and annealed siloxene, Stutzmann and co-workers^{12–14} suggested this molecule as the origin of the PS photoluminescence.

We will present evidence of a more general origin for the observed features in the form of the fluorophors associated with the silicon oxyhydrides. This suggestion concurs with the recent observations of Steckl *et al.*¹⁵ who have obtained evidence for the silicon oxyhydrides in stain etched porous silicon thin films, correlating their observations with crystallinity and photoluminescence. Further, in a study of the thermal oxidation and nitrogen annealing of luminescent PS, Yan *et al.*¹⁶ have obtained evidence that residual hydrogen exists, in a 1000 °C 10 min thermally oxidized PS film, in the form of SiOH.

With few exceptions,¹⁷ PL spectra are observed for PS samples, formed in HF solutions, which have been dried in air. Although these ex situ samples provide spectral information, their study indicates little about the evolution of the PS luminescence during the in situ etching process. We have carried out an extensive series of experiments^{3,8,18} in both aqueous [(HF/H₂O, HF/CH₃OH/H₂O, HF/C₂H₅OH/H₂O, HF/H₂O/HCl) and nonaqueous (MeCN/HF) (anhydrous)] etching media, monitoring the time-dependent PL both in situ (during the etching cycle and before the PS sample is removed from the etching solution) and ex situ (after removal of the PS from the etching solution). By correlating the ex situ with the in situ behavior of the PS, we find that the aqueous electrolyte composition plays an extremely important role in the onset, intensity, and lifetime (solution) of the PL emitters.^{3,18} Comparable studies on nonaqueous electrolytes demonstrate distinctly different correlations between the in situ and ex situ behavior and thus provide insight into the mechanism of the PL process. A range of experiments coupled with quantum chemical calculations¹⁹ suggests that the PS photoluminescence results from a silicon oxyhydridelike fluorophor strongly bound to the PS surface. Here the oxyhydride contains an Si=O double bond which may have hydrogen, hydroxide, SiH₃, or OSiH₃ ligands bound to the silicon. We can also establish that the corresponding silylenes or tricoordinated silicon compounds with a dangling electron do not contribute to the observed photoluminescence.¹⁹

Here we outline several experiments conducted in aqueous and nonaqueous media which support a surface bound molecule-like emitter as the source of the PL from porous silicon. Several observations lead us to this conclusion. We observe the early appearance in time (<10 s) of the PS luminescence consistent with the formation of a surface bound emitter created on a time scale much shorter than that necessary for pore formation.⁸ We find that a selection of laser excitations (PLE) over the wavelength range extending from 193 to 400 nm produce an almost identical *time-dependent* PL emission feature. This result, which is not consistent with quantum confinement, suggests the pumping of the excitedstate manifold of a molecule-like species followed by rapid nonradiative relaxation through the manifold and the subsequent emission of radiation at much longer wavelength.

We outline the results of detailed quantum chemical modeling¹⁹ which clearly suggest a close correlation between the manifold of silicon oxyhydride triplet (and singlet) excited states, their relation to the ground-state singlet states, and a similarity to the observed PLE excitation spectrum. Changes in bonding associated with electronic transitions involving the oxyhydride ground electronic and low-lying triplet states, especially in the SiO related bonds, and the substantial shift to larger internuclear distance of these excited electronic states relative to their ground states can easily explain the observed character of the PL spectra. The excitation to a manifold of states greatly shifted from the ground electronic state partially explains the significant redshift of the PL spectrum (600-800 nm) from the known absorption peak wavelength of the (PLE) excitation spectrum (\sim 350 nm).²⁰ In correlation with additional time-dependent studies, the results which we outline also suggest an alternate interpretation to the multiexponential PL time decay observed⁹ as a function of increasing wavelength after excitation at 355 nm. These observations, which indicate a faster decay at shorter wavelengths, have been used to support the hypothesis of a quantum confinement model in which smaller particles are predicted to have faster decay rates.²¹ However, the results of the current study suggest that this behavior (also not unique to quantized particles²²) might be the manifestation of relaxation cascade down the manifold of a polyatomic silicon oxyhydride triplet exciton.

Within the framework of the outlined quantum chemical results, we reassign the ODMR spectra^{12–14} obtained for PS and associated with a triplet exciton (which is the source of the PS orange-red emission). We associate these spectra not with a complex siloxene emitter but with an equally appropriate and simpler silicon oxyhydride-like molecular emitter possessing similar silicon-oxygen and silicon-hydroxide fluorophores. We consider recent attempts⁶ to associate the large linewidth of the triplet ODMR spectrum with an inhomogeneous distribution of quantum confined crystallites. We demonstrate that the correct extension of the arguments used in this analysis, in fact, provides clear evidence for the existence of a common radiative center associated with a molecule-like species bound to the surface of the PS framework.

II. EXPERIMENT

PS samples were prepared as a result of the anodic etching of (100) silicon wafers obtained from MEMC (Dallas, Texas). The *p*-type Si wafers were boron doped and had resistivities of 2, 15, and 224 ohm-cm. They were etched in a variety of HF based mixtures which could be grouped into HF (dilute)-MeOH, HF (conc.), HF (dilute)-H₂O, and anhydrous HF-MeCN solutions. Both *in situ* and *ex situ* experiments were conducted. In order to carry out studies of the light-induced photoluminescence from several PS surfaces both during the etching process and after removal from the etching solution, it was necessary to adopt a consistent and reproducible alignment procedure.

In order to monitor the porous silicon photoluminescence during the etching process, the silicon wafer was mounted in an optically transparent uv grade silica or plastic cuvette filled with etching solution. Ohmic contacts were made to the semiconductor by sputtering aluminum (300 nm) on the back side of the sample forming a tunnel diode. The wire, connected to the sample using conductive paint (Insulating Materials Inc., Ekote #3030), and the sputtered aluminum surface were then covered with a layer of black wax (Apiezon W), leaving only the front surface of the silicon exposed to the etching solution. Both the silicon wafer wire and platinum electrode connections passed through a Teflon cap which was tightly fit to the cuvette. For those experiments with anhydrous HF/MeCN etching solution, the cuvette was filled in a dry box (Vacuum Atmospheres Co., Hawthorne, CA) under nitrogen and the cap was sealed before transport using either vacuum grease (Dow Corning High Vacuum) or silicon caulking compound. Etching currents applied ranged from 2 to 30 mA/cm² with the majority of experiments conducted in the range $4-10 \text{ mA/cm}^2$.

The optical train for these photoluminescence experiments was arranged on an optical breadboard. Here, the output from an appropriate pulsed laser [Nd: YAG (yttrium aluminum garnet) pumped dye laser in the range 390-320 nm, nitrogen laser at 337.1 nm, and KrF and ArF exciplex lasers at 248 and 193 nm, respectively] or a cw argon ion laser was expanded and sent through a mask to the porous silicon surface. In order to excite the photoluminescence process during the etching cycle, the laser outputs traversed the etching solution and impinged directly onto the etching silicon wafers. The majority of these in situ studies used nitrogen or KrF excimer laser radiation. Since an anhydrous HF/MeCN solution strongly absorbs 248 nm (KrF) and 193-nm (ArF) radiation, only a nitrogen laser, mercury lamp, or YAG pumped dye laser could be used for these experiments. In several experiments carried out after the porous silicon samples were washed and allowed to dry in air, the observed ex situ photoluminescence was of sufficient intensity so as to warrant excitation using only the scattered light from the laser sources with no direct "focusing" of the laser onto the PS surface.

In order to carry out a readily reproducible photoluminescence study, a clear alignment procedure was adopted. It was necessary to align the photoluminescence with the entrance slit of the scanning monochromator (McPherson). The cuvette was placed into a permanent clamp holder connected to a magnetic base x-y mount attached directly to the top of the optical breadboard. After verifying that the cuvette was properly illuminated by the masked light source of choice for a given experiment, a strongly luminescent PS sample from a previous experiment was placed into the cuvette and the position of the monochromator was adjusted to maximize the photoluminescence signal at 650 nm. The direct scattering of laser light into the monochromator was avoided to the greatest extent possible. The calibrating PS sample was then removed and the cuvette filled with the appropriate etching solution. The silicon sample of interest (anode) and the Pt wire (cathode) were then placed into the cuvette. The sample was adjusted vertically to optimal alignment with the exciting laser source and rotated so as to avoid direct laser reflection into the monochromator. The leads were attached to a computer-controlled home-built constant current source and, after a final alignment check, the entire system was covered with a heavy black cloth to minimize contamination of the experiment by the room lights. Care was also taken to assure that the observed photoluminescence was excited in a singlephoton excitation process.

The photoluminescence was dispersed through the monochromator, which was scanned using a computer interfaced stepping motor, and impinged on a Hamamatsu 446 phototube. The output from the phototube was sent to an SR400 (Stanford Research Series) photon counter whose gate for most experiments was set to the first 100 μ s of photoluminescence. The output from the photon counter was processed using an IBM/PC compatible computer. The photoluminescence from the PS was studied both during the etching cycle, following etching in solution, and upon the removal, washing, and drying of the sample in air. Not only were ex situ samples studied in air but also under solutions of HCl/H₂O, methanol, ethanol, or ethylene glycol in which the washed sample was placed. These samples were placed into their original holders and sometimes also into a cuvette which contained the rinse solutions as outlined above. The previously outlined alignment procedure was also repeated. A typical scan, first from 490 to 730 nm, in 2.5-nm steps with 30-40 laser shots per data point for lasers running with repetition rates between 20 and 30 Hz, requires \sim 3.5–4 min. This scan is immediately taken in reverse, furnishing a consistent internal check for any possible changes which might occur during the scan cycle. Because of the changes which can be manifest over the 3.5-4 min scanning period, several runs were also devoted to time scans at the individual wavelengths 520, 620, and 710 nm. Spectral calibration could be accomplished with a mercury lamp or the individual laser excitation wavelengths, often in second order.

III. IN SITU PHOTOLUMINESCENCE IN AQUEOUS AND NONAQUEOUS MEDIA

A. Aqueous versus nonaqueous etch cycles

Distinctly different PS samples are generated in the aqueous and nonaqueous etching of *p*-type silicon in solution. In a nonaqueous MeCN/HF (anhydrous) etching medium it is possible to fabricate open and accessible macroporous photoluminescent PS structures with deep, well-ordered channels²³ in the absence of light (required for *n*-type silicon²⁴). This open structure is believed to result from an oxidation dissolution mechanism. Trace quantities of water are required for the onset of PL where the luminescent sites appear to form at specific crystallographic locations. Under similar conditions, with an aqueous etching process, random



FIG. 1. *In situ* PL at 620 nm for (a) MeCN/HF, (b) 20% HF in MeOH, and (c) 50% HF in MeOH. Etching current was 4 mA/cm^2 starting at time zero. The spectral intensities are normalized for comparison.

nanopores with far less accessible photoluminescent PS structures are generally formed. The observation of emission from the *nonaqueous* etched material establishes that very fine nanoporous structures are not a prerequisite to induce PL in PS.

B. Photoluminescence in the earliest stages of porous silicon formation

In fact, we have observed visible PL from both aqueous and nonaqueous etched samples prior to the formation of any pores.⁸ The development of the PL with etch time at a current density of 4 mA/cm² in a "nonaqueous" etching solution of MeCN with 2 mol/liter HF is shown in Fig. 1(a). This PL is detected within the first 10 s of the etch cycle in a solution where the concentration of water is <0.001 mol/liter. The PL increases until the etching current is terminated at which point a sharp rise in the PL intensity is observed. This result suggests that the etching process both creates and destroys surface bound photoluminescent emitters.

Visible PL is also observed at very short times when a polished silicon wafer is electrochemically etched in MeOH with 6 mol/liter HF. The concentration of water in this solution is approximately 7 mol/liter. The PL depicted in Fig. 1(b) begins within the first 5–10 s of the etching cycle, continually increasing until the etching current is terminated at 60 s. A gradual increase in the PL is then observed over a

limited time followed by a decrease in the PL as the silicon sample continues to soak in the etching solution. We find that much less than 100 nm of silicon need be removed before the luminescence centers are formed.⁸ The topographical changes in the surface are consistent with the formation of emitting, constrained surface species. Further, these results suggest the importance of an etching-solution–silicon-surface interface chemistry.

C. Chemistry at the etch-solution-silicon-surface interface

The importance of chemical changes at the silicon surface, as they influence the nature of the observed PL and correlate with etch solution variation, are also apparent in several additional experiments. At higher HF concentrations (14 mol/liter HF in MeOH [Fig. 1(c)]) a distinctly different behavior can be observed as the PL cannot be excited until \sim 25 min after the etching process has been completed. That is, no PL is observed during the etching process. After the current is terminated and the sample is left soaking in the HF solution, the PL rises after a notable gestation period. The PL then peaks and drops off in intensity over a period of ~ 1 h.⁸ All three *in situ* PL scans in Fig. 1 demonstrate a clear dropoff in PL intensity which appears to be most consistent with a surface localized dissolution process^{3,18} as opposed to oxidative quenching resulting from SiO₂ formation.³ We are able to correlate the PL intensity with the specific constituency of the etching solution and establish conditions under which the PL from PS is stabilized, enhanced, or quenched. For example, we have demonstrated¹⁸ the strong stabilizing and enhancing influence of small quantities of water on the PL emitters created in a nonaqueous etching process, the initial phases of which are described in Fig. 1(a). Further, we have observed the PL stabilizing effect of concentrated hydrochloric acid introduced in equal volume to a doubly deionized water solution in which a PS surface is photoluminescing.¹⁸ In contrast, as we monitor the time dependence of the PL emission from an aqueous HF solution, we observe that the decay of the PL is enhanced through introduction of methanol or ethanol to the solution.³ This enhanced decay is exemplified in Fig. 1(b).

Under certain conditions, PS displays a "green" luminescence during the early and intermediate stages of the *in situ* etching process. The green luminescence (~520 nm) then transforms to a final "orange-red" luminescence^{3,23,25,26} although it can be stabilized through the introduction of ethylene glycol.^{3,25} These variations of the PL with etching solution and with the introduction of various constituents to the solution suggest the importance of the chemistry of the etch solution to the PL process. The effects can be shown to be consistent with counteracting mechanisms for PL and silicon dissolution.^{18,23,27–29} These observations are not consistent with quantum confinement.

D. Correlation with surface morphology

Changes in the topography for the silicon surface etched in 6 mol/liter HF in MeOH [Fig. 1(b)] (Ref. 8) suggest only a texturing of the surface and no pore formation. With $2e^{-}/Si$, the average silicon removed in 60 s of etching was ~150 nm. With scanning force microscopy (SFM), the quantified topography after 0, 5, 10, 20, and 60 s demon-

TABLE I. 50/50 sample as function of time.

Etch time (sec) ^a	Average surface area difference (%)	Standard deviation (%)
0	0.741	0.336
5	1.329	0.267
10	2.645	0.606
60	5.489	0.940
960	3.824	0.877
2400	4.820	0.986
3600	6.180	1.689

^aTime after initial etch process began.

strates a clear and progressive roughening. Careful examination of the near-surface region, however, demonstrates⁸ that PL can be observed prior to the development of nanometer size pores. It appears also that an increase in roughness alone is not the sole origin of the PL. While the observed increase in PL intensity with etch time depicted in Fig. 1(b) [as well as Fig. 1(a)] demonstrates that the luminescent centers can be created after the appropriate topological structures have been formed, the rise and fall in PL after the electrochemical etching has been terminated suggests that electroless chemical changes may result in the enhancement and/or quenching of the PL perhaps through formation and/or dissolution of an oxyhydride [also Fig. 1(c)].

In a further SFM study, the topography of the silicon surface has been studied at various stages of the PL process, for the higher concentration 14 mol/liter HF in MeOH solution [Fig. 1(c)]. Here we have quantified the topography at times of 0, 5, 10, 60, 960, 2400, and 3600 s covering the lengthy time frame over which the PL source is first formed, reaches a maximum, and drops to a very low level. The results of this study summarized in Table I suggest a consistent increase in the roughening of the PS surface while the PL has cycled through a clear maximum and has been virtually quenched. This result, in concert with the outlined previous study,⁸ suggests that surface roughening is a necessary but not sufficient condition for PL emission. This again points to the creation and dissolution of a surface bound emitter which we will suggest is a silicon oxyhydride-like molecule.

IV. PHOTOLUMINESCENCE AS A FUNCTION OF LASER EXCITATION WAVELENGTH

A. Summary of in situ behavior

The "green" luminescence^{25,26} which PS displays during the early and intermediate stages of the etching process is considerably more pronounced in an aqueous etching cycle at moderate HF concentrations (20% HF in MeOH). The transformation from "green" to "orange-red" luminescence is easily followed and can be impeded for several hours if the etched sample is placed in an ethylene glycol solution.^{3,25,26} The "green" and "orange" emitters appear to be distinct surface entities which are selectively excited by the light sources used in these experiments. Upon removal from the etching solution, before drying, a freshly etched sample appears green under Hg lamp excitation but "orange-red" when excited by a KrF or ArF laser. After the PS sample matures in air for a considerable period, its transformation to an orange-red emitter is complete and all illuminated regions bear the orange-red luminescence regardless of the uv excitation wavelength.

The green and orange-red emissions have been previously assigned to interlocking exciton fluorescence and phosphorescence emissions, respectively.^{4,5} However, the series of *in situ* pump excitation experiments with nitrogen and KrF lasers and a Hg lamp begin to establish an intimate relationship between the green and orange-red luminescence and suggest that the green emission emanates from a precursor state which is chemically transformed to the final red emitter.²⁶ An intersystem crossing process involving these two emitters, as suggested by others,⁴ seems far less likely. Although the overlap of the emission ranges for the green and orange-red emitter, the emission rates appear comparable for these two emission sources.³⁰

B. Ex situ photoluminescence excitation spectroscopy

In this section we discuss a series of laser excitation experiments on mature PS samples which have been etched for 10 min at 4 mA/cm^2 , removed from the etching solution, rinsed thoroughly in methanol, and dried in air. While the effect of this process is dominated by the changes which the etching process and the etching solution produce on a PS surface, changes produced at the PS surface by the laser must be also considered. At sufficient fluxes, the output from an ArF (193 nm) laser impinging on a photoluminescent PS surface will rapidly destroy the PL. This suggests that the laser is capable of *thermally desorbing* emitting fluorophors from the PS surface and that limited fluxes are certainly warranted. The problem does not appear to be as significant for longer wavelength excitations involving KrF (248 nm), N₂ (337 nm), or Nd:YAG pumped dye laser pumping. Nevertheless, we have attempted to monitor the power dependence of the in situ PL emissions observed in this study. For the mature samples that we consider, the observed ex situ spectra within a given time profile do not shift with increasing laser power. The PL intensity scales linearly with incident laser flux as the experiments are not driven by multiphoton processes.

C. Surface-confined versus quantum-confined emitter

An analysis of the temporal behavior of the PL decay and the characteristic PL emission spectra observed during and after the formation of the PS surface can assist in assessing the species responsible for the observed emission. In complement to the dispersed PL spectrum, a detailed analysis of the excitation spectrum (PLE) associated with the prepared PS surfaces can be used to distinguish between the inhomogeneous broadening and multiple spectral profiles which should be associated with quantum confinement and the contrasting emission from fluorophors physisorbed or chemisorbed (trapped) on the PS surface. If the observed PL emission spectrum is inhomogeneously broadened and results from the overlap of a large distribution of emission spectra from individual quantum particles as would be associated with quantum confinement, the emission associated with the excitation spectrum should change in shape significantly as the monitoring emission wavelength changes. This should be particularly apparent at the shorter wavelength edge of the emission and at low temperatures. In contrast, if the emission arises from one or more molecular entities located on the PS surface, the excitation spectrum should be characterized by one or more thresholds located at higher frequency than the highest frequency of the resulting emission spectrum. Furthermore, the shape of the spectrum should not change as the excitation wavelength which induces the emission is changed. This is precisely the behavior, as a function of laser excitation wavelength, that we observe.

The emission observed from a PS surface, whether from an inhomogeneous distribution of quantum-confined crystallites or from a group of molecule-like surface-based fluorophors, will display a similar temporal behavior. This is true whether or not the observed emission results from the spectral diffusion that might be associated with an inhomogeneous distribution or the relaxation down an "excited state" manifold. Therefore, it is important that one specify the PL emission sampling time gate.

In Fig. 2 we present laser-induced PL emission spectra for a small number of similarly prepared samples. We find that excitation across the visible and ultraviolet spectral regions from 388 to 193 nm produces a nearly identical PL emission. With one notable exception, these spectra (Fig. 2) were all taken with time gates between 0 and 100 μ s. The spectrum pumped at 348.3 nm was sampled from 0 to 0.1 μ s and shows a clear blueshift relative to the other scans. This observation of virtually identical PL spectra as a function of laser excitation wavelength suggests that the source of the PS luminescence is a surface-based emitter or fluorophor and not a quantum-confined crystallite of silicon. Further, the creation of pores appears to have a minimal effect on the PL intensity distribution and excitation profile.

The nature of the observed photoluminescent spectra, especially the blueshifted 348.3-nm excitation–PL spectrum, in conjunction with the quantum chemical calculations which we outline in the following section, provides evidence for the relaxation down a pumped excited-state triplet manifold with subsequent emission from the lower levels of this manifold. These data, in turn, suggest an additional experiment based upon the substantial shift of the potentials describing the exciton triplet excited state to which we pump in the present experiments.

If the triplet exciton first identified by Stutzmann and co-workers^{12–14} is significantly shifted relative to a ground electronic state singlet, a laser pump from this ground state will be to levels higher up the excited-state potential (Fig. 3). This will be followed by a relaxation, determined by the complex mode structure of the excited state, and by subsequent emission at much longer wavelengths. These are precisely the characteristics demonstrated by the significant difference in the peak of the PS-PLE spectrum at ~350 nm (Ref. 20), and the PL emission wavelength range from ~600 to 800 nm. Further, it should be noted that the PL spectra which we generate on the 0–100 μ s time scale in Fig. 4 will be redshifted with increasing gate time.

Based upon the suppositions which we have presented, we suggest that two lasers at very different wavelengths and energies will access very different regions of the exciton trip-



FIG. 2. Laser-induced photoluminescence emission spectra as a function of a varying excitation wavelength (PLE- λ) from 193 to 388 nm. The porous silicon samples obtained as 2 Ω cm wafers were etched at 10 mA/cm² for 4 min in a 20% HF in MeOH solution (MeOH with 6 mol/liter HF, ~7 mol/liter H₂O). The spectra were taken at room temperature in air using samples rinsed in doubly ionized water and methanol and subsequently dried. The spectrum pumped at 348.3 nm was sampled from 0 to 0.1 μ s, whereas all other spectra were taken over the time gate 0–100 μ s. See text for discussion. Spectral intensities (a)–(g) are individually normalized for comparison.



Si = O Bond Distance

FIG. 3. Schematic of silicon oxyhydride ground-state singlet and excited-state triplet potentials indicating (1) the possible origin of the substantial difference in photoluminescence excitation (PLE) and subsequent photoluminescence (PL) emission energies and (2) the distinction between an ArF excimer laser and nitrogen laser pump of a porous silicon sample.

let potential. The net effect on the observed temporal profile of the observed emission will depend upon the relative rates of nonradiative relaxation within the excited-state manifold and the emission rate. If the excited-state emission rate is very much slower than the nonradiative relaxation rate, two widely separated pump energies will produce PL emissions that (1) are not clearly separated in time and (2) likely emanate from the lowest rovibronic levels of the electronic excited state. If the emission rate is very much faster than the relaxation rate, we should observe photoluminescence at wavelengths very similar to the pump energy. This is clearly not the result of the experiments summarized in Fig. 2. If, however, the emission rate and relaxation rate are comparable, we expect to observe a separation in the temporal profiles resulting from well-separated pump energies.

In Fig. 4, we present temporal scans of the PL emission produced from PS surfaces, generated using a 20 % HF in methanol etch solution at 4 mA/cm^2 [(10 min), rinsed in methanol and dried in air] as these surfaces are pumped by ArF [193 nm ($\sim 51\ 800\ cm^{-1}$)] and N₂ [337 nm $(\sim 29\ 675\ cm^{-1})$] lasers. As Fig. 3 indicates, the ArF laser will pump higher on the excited state manifold. For gates of 1-2 [Fig. 4(a)], 2-3 [Fig. 4(b)], or $3-4 \mu s$ [Fig. 4(c)] we observe a clear separation of the PL emission spectra with the ArF spectra clearly blueshifted. The separation also would appear to be decreasing slightly as a function of increased gate time. The energy separation $\sim 20\ 000\ {\rm cm}^{-1}$ between the two lasers is substantial suggesting that the electronic emission rate lags the excited-state internal relaxation rate but that the two are not on vastly different time scales. The time scale of these experiments then suggests an excited-state radiative lifetime of order several microseconds. This experiment also suggests that the PL emission spectra depicted in Figs. 2 and 4 do not emanate from the lowest excited-state levels.

V. QUANTUM CHEMICAL MODELING OF THE SILICON OXYHYDRIDES

In order to assess whether the source of the PS photoluminescence could be a silicon oxyhydride-like fluorophor strongly bound to the PS surface, we have carried out a detailed quantum chemical study¹⁹ of several model compounds. We have extended two previous studies^{31,32} of the molecular electronic structure of silanone [Si(O)H₂] and the OH (for H) substituted silanoic [Si(O)H(OH)] and silycic [Si(O)(OH)₂] acids. Here, in addition, we study Si(O)H(OSiH₂), Si(O)(OH)(SiH₂), and Si(O)(SiH₂)₂ as models for sites present on the surface of an etched silicon wafer (see also Tables II–IV).

The results obtained suggest, as Table II indicates, that the triplet excited states of the silicon oxyhydrides are located in energy regions consistent with the observed peaks in the PS photoluminescence excitation spectrum. The calcula-



FIG. 4. Temporal scans of the photoluminescence emission produced from PS surfaces prepared from a 2- Ω cm silicon wafer using a 20% HF in methanol etch solution and a current density of 4 mA/cm² for 10 min. The samples, rinsed in methanol and dried in air, were pumped by ArF (193 nm, ~51800 cm⁻¹, gray) and N₂ (337 nm, ~ 29675 cm⁻¹) lasers and the photoluminescence was sampled for time gates of (a) 1–2 μ s, and (b) 2–3 μ s, and (c) 3–4 μ s. The spectra display a clear separation of the PL from ArF (blueshift) and nitrogen laser excitation. The sharp dip in (a) corresponds to the saturation of the *R*636 phototube used to detect the PL. See also text for discussion.

(HO)HSiO
$$\rightarrow$$
 triplet $\Delta E = 70.9 (\lambda = 403 \text{ nm})$

Si = O

Si = O

Si = O

(HO)₂SiO
$$\rightarrow$$
 triplet $\Delta E = 71 (\lambda = 402 \text{ nm})$

(SiH₃O)HSiO → triplet ΔE = 70.3 (λ=406 nm)
$$H_3SiO$$

H³SiO Si = O

(SiH₃)HSiO
$$\rightarrow$$
 triplet Δ E = 57.3 (λ =499 nm)

$(SiH_3)(HO)SiO \rightarrow triplet \Delta E = 71.2 (\lambda=401 nm)$

tions also suggest a close correlation between the manifold of silicon oxyhydride triplet excited states and the observed green and "orange-red" PL spectra.²⁶ Further, the demonstrated changes in bonding associated with electronic transitions involving these species, especially in the SiO related bonds, correlate well with the observed character of the PL spectra.

We have employed both *ab initio* molecular orbital (MO) theory and density-functional theory (DFT for ground-state singlets) using the program systems DGAUSS (DFT calculations) and GAUSSIAN 94 (*ab initio* MO calculations).^{33,34} The molecules Si(O)H₂, Si(O)H(OH), Si(O)(OH)₂, Si(O)H(OSiH₃), Si(O)H(SiH₃), Si(O)(OH)(SiH₃), and Si(O)(SiH₃)₂ were used as models for the various sites that might be present on a hydrogen-passivated silicon surface³⁵ undergoing oxidation. Although cluster models such as these do not include the long-range Coulomb effects present in the bulk, they can provide useful insights into the effect of changing the functional groups which are attached to the silicon.

Optimized geometries at the DFT level have been evaluated for the ground-state singlet and lowest excited triplet state using a polarized triple-zeta basis set.³⁶ Second derivative calculations demonstrate that these structures represent minima.³⁷ These optimum geometries were then used in molecular orbital calculations at the Moller-Plesset 2 (MP2) level³⁸ with a polarized double-zeta basis set.³⁹ Geometries were reoptimized at the MP2/double zeta with polarization (DZP) level and frequency calculations were done for these optimized geometries. In order to evaluate corrections to the singlet-triplet separations determined at the MP2/DZP level, higher-order correlation calculations were done on Si(O)H₂ at the optimized geometries. These calculations were done at the CCSD(T) level⁴⁰ with a triple-zeta basis set⁴¹ augmented by two sets of polarization functions on all atoms and by ffunctions on the heavy atoms.

The most relevant results of these calculations are summarized in Tables II–IV. A detailed description is given elsewhere.¹⁹ In Table III we summarize the Si=O bond lengths determined for the ground-state singlet and low-lying

2145

TABLE III. Si=O bond lengths (Å) for silanones at the MP2/DZP level.

Molecule	r(Si=O) singlet	r(Si=O) triplet	$\Delta r(Si=O)$
Si(O)H ₂	1.545	1.700 ^a	0.155
Si(O)H(OH) ^b	1.537	1.709	0.172
Si(O)(OH) ₂	1.536	1.709	0.173
Si(O)H(OSiH ₃)	1.537	1.708	0.171
Si(O)H(SiH ₃)	1.553	1.695	0.142
Si(O)(OH)(SiH ₃)	1.543	1.712	0.169
Si(O)(SiH ₃) ₂	1.560	1.681	0.121

^aBond length for the excited singlet is 1.705 Å.

^bBond lengths for HO-Si-OH silylene are 1.670 Å for the groundstate singlet and 1.680 Å for the excited triplet.

excited-state triplet of the model compounds considered. These calculations demonstrate a significant change in the excited triplet state bonding relative to the ground state, localized largely in the Si—B bonds. In contrast, for the model compounds considered, changes in the Si-Si bond distance (Table V) (Ref. 19) are of a much smaller order (0.005–0.02 Å). The data in Table IV indicate the calculated singlettriplet separations for the model silanone compounds of interest all of which are consistent with the porous silicon PLE spectrum.

It is noteworthy that the locations of the unsaturated silicon oxyhydride excited triplet states and the known peak wavelength of the porous silicon (PLE) excitation spectrum $(\sim 350 \text{ nm})$ ²⁰ both bear a clear resemblance to the known singlet triplet splittings of the low-lying silicon monoxide intercombination band systems⁴² which occur in nearly the same energy region. The large change in the SiO bond lengths indicated in Table III, in turn, produces a large shift in the excited-state potentials relative to the ground state, consistent with a significant difference in the peak of the PLE excitation spectrum (~350 nm) and the observed PL emission range [~500-550 nm (green), ~600-800 nm (orange)]. The data are also consistent with excitation pumping high up the excited-state triplet manifold followed by subsequent relaxation within the excited-state manifold before emission.

TABLE IV. Ground-state singlet-excited energy separation for silanones (silylenes).

Molecule	$\Delta E(S-T)$ (kcal/mol)	$\begin{array}{c} \Delta E(S\text{-}T) \\ (\text{eV}) \end{array}$	$\sim \lambda_{Adiabatic} (nm)$
Si(O)H ₂	60.1	2.61	475
Si(O)H(OH)	70.9	3.07	403
Si(O)(OH) ₂	71	3.08	402
Si(O)H(OSiH ₃)	70.3	3.05	406
Si(O)(OH)(SiH ₃)	71.2	3.09	401
Si(O)H(SiH ₃)	57.3	2.48	499
Si(O)(SiH ₃) ₂	53.9	2.34	530
HSiOH	38.4	1.66	744
HOSiOH	64.2	2.78	445
SiH ₃ OSiOH	67.3	2.92	425

TABLE V. Si-Si bond lengths (Å) for silanones at the MP2/DZP level.

Molecule	r(Si-Si) singlet	r(Si-Si) triplet	Δr (Si-Si)
$Si(O)H(SiH_3)$	2.354	2.361	0.007
$Si(O)OH(SiH_3)$	2.342	2.365	0.023
$Si(O)(SiH_3)_2$	2.366	2.363	0.003

There are additional striking trends which are associated with the data of Tables III and IV. First, we note that whenever an OH or OSiH₃, (OR), group is bound to the siliconoxygen bond, the change Δr (SiO) is consistently of order 0.17 Å. Further an additional OH group does little to affect this differential change in bond length accompanying the singlet-triplet transition. In the absence of an -OH or -OR group this change is notably smaller, decreasing from 0.155 Å for Si(O)H₂ to 0.121 Å for Si(O)(SiH₃)₂. These are distinct differences associated with an -OR versus R group bonding to the silicon. Further, we note the very similar adiabatic energy differences, $\Delta E \approx 3.05$ eV, which characterize those singlet-triplet transitions where an OH or OR group is bound to the Si=O moiety. Contrast these virtually identical energy increments to the much lower and decreasing adiabatic energy differences associated with the series $Si(O)H_2(0.155), Si(O)H(SiH_3)(0.142), Si(O)(SiH_3)_2(0.121)$ where the smaller change, $\Delta r(SiO)$, in the SiO bond length will lead to a smaller redshift of the PL emission feature. These results thus indicate that the oxyhydrides with bound -OR ligands will produce a much larger redshift of the PL emission spectrum relative to the peak of the PLE excitation spectrum than those fluorophors having only R group ligand binding. We suggest that the magnitudes of these changes are relevant to the correlation of the mechanism for PS formation with the assignment of the transforming green and final orange-red photoluminescence emissions.²⁶ We associate the green emitter with an R group bound fluorophor and the orange emitter with the oxidative insertion into an SiH $(\rightarrow$ SiOH) or Si-SiH_r (SiOSiH_r) bond.

VI. THE NATURE AND INTERPRETATION OF OPTICALLY DETECTED MICROWAVE DOUBLE RESONANCE EXPTS

Stutzmann and co-workers^{12–14,43} have used the ODMR to examine the microscopic nature of the excited-state responsible for the strong visible PL in porous silicon. Their observation of *sharp* dipole forbidden $\Delta m = \pm 2$ transitions (Fig. 5) in the ODMR spectrum represents the clearest proof that the excited state is a triplet exciton. The allowed $\Delta m = \pm 1$ transition, with the characteristic shape of a Pake doublet⁴⁴ has been associated with a spin-spin interaction with linewidth ≈ 500 G *independent of the photon energy monitored*. Stutzmann and co-workers have argued that the triplet exciton states responsible for radiative processes in porous silicon and in annealed siloxene (Fig. 5) provide strong evidence for a common radiative center. With the assignment of the $\Delta m = \pm 1$ linewidth to a spin-spin interaction



FIG. 5. Comparison of the ODMR spectra for porous silicon and annealed siloxene. See text for discussion.

tion, these authors conclude that the exciton diameter, determined within the dipolar approximation, is of order 4 Å. These authors suggest that the spin-spin separation, which might be associated with Si₆ rings, is qualitatively incompatible with geometric quantum confinement, pointing to a molecular origin of the radiative center. In contrast, Nash *et al.*⁶ have argued that the broad $\Delta m = \pm 1$ feature (Fig. 5) might best be assigned to a second-order spin-orbit interaction which can dominate the dipolar process and that this dominance might lead to the prediction of interaction distances of order 30 Å compatible with quantum confinement.

We will argue that the model proposed by Nash *et al.*⁶ would appear to lose validity if expanded to consider the effect of the spin-orbit interaction as it leads to a broadening of the $\Delta m = \pm 2$ transitions. The absence of this broadening in the experimentally observed ODMR spectrum in fact argues against quantum confinement and for a localized molecular center. Further, the arguments presented by Stutzmann and co-workers might also be modified.

Annealed siloxene is obtained from as-prepared siloxene, with the destruction of its two-dimensional silicon planes, through oxygen insertion and the formation of strongly disordered silicon-oxygen-hydrogen networks dominated by localized states.⁴⁵ In concert with the previously outlined results and with the data presented by Steckl *et al.*¹⁵ and Yan *et al.*¹⁶ we will argue that the suggested association of the spin-spin separation with Si₆ rings is not appropriate and should be modified through consideration of the silicon oxyhydride fluorphors present in both PS and annealed siloxene. Indeed Brandt and Stutzmann¹⁴ and Zacharias, Dimova-Malinovska, and Stutzmann⁴⁶ have noted that ODMR spectra very similar to those of PS and annealed siloxene are observed in hydrogenated amorphous silicon suboxide alloys.

The spin Hamiltonian for the lowest-lying exciton triplet, to first order in perturbation theory is⁴⁷



FIG. 6. Splittings for the lowest-energy triplet exciton of porous silicon. (a) The threefold spin degeneracy is split by the second-order spin orbit interaction and (b) the splitting of the $m=0, \pm 1$ sublevels by a magnetic field *B*. See text for discussion.

$$H = \sum_{i,j} D_{i,j} S_i S_j + \mu_B \sum_{i,j} g_{i,j} B_i S_j, \qquad (1)$$

where the first term is the zero-field splitting and the second is the linear Zeeman term, and where the i,j correspond to Cartesian components, D_{ij} is the fine-structure tensor which differs with the structure of a given exciton triplet, S_i corresponds to the spin operator for spin unity, B is the magnetic field, μ_b is the Bohr magneton, and g_{ij} is the "g tensor" for a given exciton triplet. The fine structure tensor D_{ij} , results from two distinct contributions, the magnetic dipole-dipole interaction of an electron and hole and the second-order spinorbit interaction. The spin-orbit contribution will dominate the dipole-dipole interaction provided that the orbital angular momentum is not quenched for an excited state of sufficiently long radiative lifetime.¹²⁻¹⁴

For large B fields, the D_{ij} are treated as a perturbation in Eq. (1). The unperturbed states correspond to m = 1, 0, -1states (Fig. 6) of normalized nS projected spin components with $n_i = \sum g_{ii} B_i$. The first-order shift of the zero-field levels with B field is the same for the m = +1 and m = -1 levels but different for m = 0 (Fig. 6). The m = -1 to m = +1 transition $(\Delta m = 2)$ is therefore unperturbed by D_{ii} and is sharp for a single triplet exciton. In contrast the m=0 to m= $\pm 1(\Delta m = \pm 1)$ transitions are perturbed by D_{ii} which also differs for each exciton. For a single triplet exciton, differing spatial orientations of the spin with respect to B field (nS)will produce a broad overall feature for the $\Delta m = \pm 1$ transition region and a sharp $\Delta m = \pm 2$ transition feature as is apparent from Fig. 5.48 However, while a distribution of triplet excitons confined by structures with a variety of shapes, sizes, and orientations with respect to the B field clearly also produces a broad overall feature for the $\Delta m = \pm 1$ transition region, this must be accompanied by a significant broadening corresponding to a distribution of $\Delta m = \pm 2$ transition features associated with the variance of D_{ii} as a function of the shape and size of the exciton structures. This latter important consideration has been neglected by Nash et al.⁶ in their critique of the interpretation which Stutzmann and co-workers^{12–14} give for the ODMR spectrum.

Nash *et al.* argue, correctly, that only if the second-order spin-orbit interaction is negligible can D_{ij} be attributed exclusively to dipolar coupling (or exchange coupling). These comparisons, however, focus attention on the linewidth of



FIG. 7. Linewidth of the $\Delta m = \pm 1$ transitions and the corresponding dipolar distance as a function of wavelengths determined by cutoff filters for porous silicon and annealed siloxene. The broadening is found to be independent of the particular wavelength used in the ODMR measurement.

the broad $\Delta m = \pm 1$ transition feature and neglect the wavelength dependence of the $\Delta m = \pm 2$ transition region. It is the combination of both features which must be considered. The data obtained by Stutzmann and co-workers^{12–14,43} (Fig. 7) for $\lambda_{ex} = 457 \text{ nm}$ (2.712 eV) demonstrate that the ODMR linewidth for the $\Delta m = \pm 1$ transition does not depend on the particular luminescence energy (wavelength) monitored. This result holds also for the $\Delta m = \pm 2$ transitions and for pump energies greater than 2.5 eV.49 As Nash et al.6 have noted, the D_{ii} fine-structure splitting is proportional to the exchange splitting, Δ , defined by Calcott *et al.*,⁴ which varies considerably over the photon energy range from 1.7 to 2.3 eV and is predicted to increase steadily in proportion to excitation source pump energy.⁵⁰ As Calcott *et al.*⁴ have noted, the upshift in band-gap energy splitting due to quantum confinement is proportional to L^{-2} (*L* is the interaction distance) whereas the exchange splitting is proportional to L^{-3} .⁵¹

Quantum confinement suggests a luminescence energy determined by the excitonic radius that is proportional to L^{-2} . If the orbital angular momentum is quenched, the same confinement should lead to a strong variation of the $\Delta m =$ ± 1 transition linewidth with $\Delta H \propto L^{-3}$ (dipolar coupling with $\Delta H = \mu_0 g \mu_B / 4 \pi L^3$ or $\Delta H \propto \exp(-r/r_0)$ (exchange coupling), neither of which is observed. Note also that the exchange splitting is proportional to L^{-3} . Thus, the lack of a dependence of the ODMR signal on wavelength is incompatible with a geometric quantum confinement approach. Further, the observed spectrum is also inconsistent with the assignment of the $\Delta m = \pm 1$ transition region broadening to a "second-order" spin-orbit interaction over a distribution of quantum confined silicon crystallites as the $\Delta m = \pm 1$ broadening will also be accompanied by a significant broadening of the $\Delta m = \pm 2$ transition region which is not observed. Nash *et al.*⁶ have suggested that it would be desirable to confirm this lack of a wavelength dependence with monochromated PL instead of a wavelength selection with lowpass filters. In fact, the broad band filtering used by Brandt and Stutzmann¹⁴ will prejudice the data so as to produce a greater spread in the data of Fig. 7 should these data be obtained for an inhomogeneous distribution. These arguments thus suggest a localized molecule-like origin (fluorophor) for the radiative center in PS or a signal which results from spin-spin interactions among similar fluorophors at varying surface sites.

VII. DISCUSSION

A. The question of localized moleculelike centers or defect sites

We have considered a series of experiments in aqueous and nonaqueous media that, when correlated with quantum chemical calculations, suggest that the source of the visible photoluminescence from porous silicon is a surface or defect site bound silicon oxyhydride-like fluorophor. Those "best fit" silanone based oxyhydride structures summarized in Table IV, which contain either an OSiH₃ or OH group, all display adiabatic singlet-triplet separations in the range very close to 400 nm. If we consider the large shift in the excited triplet versus ground-state singlet Si=O bond distances (outlined in Table III and diagrammed schematically in Fig. 3), we expect that the maxima in the PLE spectrum, obtained by pumping at room temperature from the lowest levels of the ground electronic state, will be shifted to considerably shorter wavelength than the ~ 400 nm value corresponding to the adiabatic energy. The peaking of the PLE (excitation) spectrum at \sim 350 nm, as has been observed by several researchers,^{9,20} is therefore completely consistent with the expected behavior of oxyhydride-like fluorophors. Further, the large shift in the excited-state triplet is expected to produce a considerable redshift of the PL emission spectrum (Figs. 2-4) relative to the excitation wavelength, again completely consistent with observation.^{9,26} Finally, as we will consider shortly, the calculated IR spectra for the silicon oxyhydrides are consistent with the IR spectrum of PS.

In effect, the oxyhydride fluorophors which we suggest represent localized centers that would be similar in form to the localized surface defects (or centers) associated by Prokes and co-workers^{2,52} with the region of the PS surface from which the orange-red PL originates. Prokes and co-workers^{2,52} have constructed a model to account for the PS photoluminescence in which they consider the role of interfacial oxide-related defects in the form of nonbridging oxygen-hole centers (NBOHC). Key support for this model has been obtained from electron spin resonance (ESR) experiments.⁵² As a function of various chemical treatments in freshly formed PS, one observes a direct correlation between the room-temperature orange-red PL intensity and the shallow donor (SD) NBOHC signal. When subjected to a short high-temperature oxidation, the SD signal can be made to disappear as it is replaced by an ESR signal associated with a center consisting of a silicon vacancy in a nearinterfacial oxide layer associated with highly oxidized silicon wafers in the bulk. As a function of various high-temperature oxidations, the signal from this latter center and the orangered PL intensity are observed to track remarkably well. The correlation between the formation, maximization, and depletion of these defect sites and the expected behavior of the surface bound silanones is striking. Prokes and co-workers^{2,52} have also used laser annealing to show that the orange-red PL cannot be a function of the silicon crystal structure since it does not track the silicon gap at high temperatures. The results, of course, suggest a molecular or defect state which is not tied to the silicon gap and therefore cannot be associated with quantum confinement.

B. Colloidal silicon suspensions and the oxyhydrides

The recent results of Henglein and co-workers^{53,54} in their study of luminescent colloidal silicon particles prepared from oxide coated crystalline silicon formed in the combustion of silane are relevant to our discussion. Henglein and coworkers found that the orange-red PL could be activated by the aqueous HF etching of the silicon particles suspended in a 1:1 cyclohexane-propanol-2 solution in the presence of air. The required presence of oxygen (under argon there is no luminescence) in these solution phase studies appears to indicate that the oxide layer created in the combustion of silane does not promote luminescence. Rather, as Heinglein and co-workers note, the development of the orange-red PL in nonpolar cyclohexane suggests that this original oxide layer must first be removed by HF. The silicon particles, with a nonpolar surface, are created in the cyclohexane phase. Here an equilibrium is established between their surface oxidation and reduction by O₂ and HF, respectively. Near-pristine silicon colloidal particles are formed whose oxidation, to a much lower level than the original oxide coated particles, produces luminescence in a process which must compete with an eventual dissolution through SiF_4 formation.^{18,23,27,28}

Based upon a study⁵³ of the quenching of the luminescence in polar solvents, trimethylamine, ammonia, and sulfuric acid and the apparent stabilizing effects of nonpolar solvents,^{3,18,23} Fojtik and Henglein⁵³ have suggested the importance of the protolytic equilibria between the three surface structures,



with the neutral hydroxyl structure corresponding to that species that can be expected to produce orange-red luminescence. Thus, these authors suggest that the orange-red PL occurs when colloidal silicon particles carry only a limited component of oxidized centers and that the protonation state of these centers strongly affects the luminescence. This result is quite consistent with the formation of a silicon oxyhydride constituency with a required OH or OR ligand.

C. The multiexponential decay of the photoluminescence from porous silicon

Bsiesy *et al.*⁷ and Xie *et al.*⁹ have studied the time resolved PL emission from porous silicon films after pulsed laser excitation. Xie *et al.*⁹ observe the multiexponential time decays depicted in Fig. 8 with apparent faster decay rates monitored at higher energies. These results have been



FIG. 8. Time resolved photoluminescence for porous silicon films at several wavelengths using a 5 nm band pass. Data are from Ref. 9. See text for discussion.

invoked^{5,9} as support for quantum confinement where smaller particles are predicted to have faster decay rates.⁵⁵ However, this behavior, which is not unique to quantized particles,²² can be expected of any localized radiative center or defect state, including the fluorphors associated with siloxene derivatives. The combination of the observed timedependent behavior,⁵⁶ the selective excitation of the green and orange-red luminescence,²⁶ and the correlation of these experimental observations with quantum chemical studies¹⁹ of the oxyhydrides suggests that the observed behavior might be the manifestation of relaxation cascade down the manifold of a polyatomic silicon-oxyhydride-like triplet exciton.

To establish an alternate interpretation, we need to evaluate further the nature of the experiment performed by Xie *et al.*⁹ The data in Fig. 8 were obtained as porous silicon films were irradiated with >1 mW of 355-nm radiation, at the peak in the PLE excitation spectrum, in 65-ps pulses.⁵⁷ The decays were evaluated on the basis of the average of 2000 laser shots. As Xie *et al.*⁹ note, the data in Fig. 8 suggest that the decay times for different wavelength emissions are all on the order of microseconds. The data presented in Fig. 2–4 are certainly consistent with this conclusion.

Xie et al.⁹ suggest that the decay times become shorter with decreasing emission wavelength (or increasing energy), and plot the emission energy dependence for these multiexponential decays as a function of a parametrized time at which the intensity decreases to 1/e of the peak value indicated at various wavelengths in Fig. 8. These authors suggest that the multiexponential decay results from radiative recombination occurring through a distribution of localized crystallite states. However, the data that we provide in Fig. 2 as we characterize the PL spectrum as a function of PLE energy, the nature of the distinct excitation associated with the green and orange-red²⁶ PL from porous silicon, the outlined quantum chemical calculations,²² and the ODMR experiments of Stutzmann and co-workers suggest that the PL correlates with stages of relaxation down a triplet exciton excited-state manifold. We suggest that the observed decay at wavelengths longer than the pump excitation wavelength will be determined by the combination of relaxation down the manifold of the polyatomic emitter and the radiative rate. In other words, the rates of cascade, determined by the flow of energy through the complex excited-state mode structure, during the radiative decay process, can greatly influence the observed time-dependent emission intensity. This effect must become more dominant as the triplet exciton undergoes its nonradiative relaxation down the excited-state manifold. If those levels that emit at progressively longer wavelengths are populated nonradiatively *during the decay process*, their apparent 1/e decay rates will be progressively reduced as well. An explanation based on cascade effects can therefore provide an alternate interpretation for the data presented in Fig. 8. We note also that some recognition of the potential role of cascade effects has been presented by Laiho, Pavlov, and Tsuboi⁵⁷ although the rate equations presented by these authors are restricted to only transitions among a few levels.

D. Infrared signatures of the silicon oxyhydrides

Xie et al.9 have obtained Fourier transform infrared (FTIR) spectra for PS films both freshly prepared and aged in air observing strong absorptions for the as-prepared samples near 2100, 914, and 640 cm^{-1} . These correspond to the stretching, bending, and wagging vibrations of SiH_r. Upon aging the PS sample in air, a feature associated with the Si-O-Si moiety at $\sim 1100 \text{ cm}^{-1}$ grows and eventually dominates the IR spectrum. This band is also accompanied by new features observed at 2250, 2200, and 870 cm^{-1} as well as features that are attributed to hydroxyl groups attached in various configurations to silicon. Dubin, Ozanam and Chazalviel58 monitor the formation of silicon oxide during the period in which they activate electroluminescence. With increasing anodization, they find that the SiH_x (x = 1-3) bands in the 2100 cm⁻¹ region decrease, while the $O_x \text{SiH}_x$ bands in the 2150–2300 cm⁻¹ region and the ν (Si-O-Si) band in the 1050-1250 cm⁻¹ range grow. Also consistent with these observations are the FTIR spectra obtained by Hory et al.⁵⁹ in their monitoring of PS passivation during post treatments which include anodic oxidation. In all cases, a clear indication of oxide formation and the subsequent oxidation of SiH_r bonds is obtained.

In Table VI, we summarize calculated infrared frequencies, intensities, and assignments for the ground states of two of the more complex silanones considered in Tables III and IV having either an OH or OSiH₃ ligand bound to the Si=0moiety. frequencies The calculated for Si(O)H(OSiH₃) and Si(O)(OH)(SiH₃) are quite consistent with the range of frequencies observed by Xie et al.,⁹ Dubin, Ozanam, and Chazalviel⁵⁸ and Hory et al.⁵⁹ All of the infrared studies indicate an oxidation signaling SiO stretch region and the development of a feature in the $870-890 \text{ cm}^{-1}$ range.9,58-60 The silanones cataloged in Tables III and IV display calculated Si=O stretch regions in the range $1125-1247 \text{ cm}^{-1}$ (Ref. 61) and a dominant $870-900 \text{ cm}^{-1}$ mode, which in the presence of an OH or OSiH₃ ligand appears to be associated, at least in part, with a combined Si-O stretch+H-Si-O(H-O-Si) bend, consistent with the observations of several workers.^{9,15,59} However, we must note that Zacharias, Dimova-Malinovska, and Stutzmann⁶⁰ have studied the behavior of the 880 cm⁻¹ band in hydrogenated amorphous silicon suboxide alloys, finding a minimal dependence on deuteration and therefore ascribing the feature to a nonhydrogen related origin. The assignment of this mixed mode feature thus appears complex.

The calculated frequency ranges for those silanones cataloged in Tables III and IV would suggest that not only a ν (Si-O-Si) stretch contributes to the 1050–1250 cm⁻¹ range but also the Si=O stretch. As we will consider,⁶² this range of the Si=O stretch frequency would appear to be manifest in several stages of silicon surface oxidation. We have also obtained evidence that indicates that the absorption of O_2 onto the silicon surface (in air) may lead to the formation of $O_2^{-.63,64}$ With a ground-state vibrational frequency, $\nu(O_2^{-}) = 1100 - 1150 \text{ cm}^{-1}$, ⁶⁴ the IR absorption of the O_2^{-1} molecule confined to a porous silicon surface may also represent a contribution to the growing 1100 cm⁻¹ feature observed by Xie et al.⁹ for their samples aged in air. Finally, we note the significant number of low-frequency modes that are associated with the silanones cataloged in Table VI. We are especially drawn to the $\sim 150 \text{ cm}^{-1}$ features that not only are effectively associated with an Si-Si=O bend, likely present in an oxidizing PS environment, but also lie very close in energy to the transverse-acoustical (TA) phonon mode in bulk silicon.⁶⁵

E. The question of quantum confinement

Our studies of the photoluminescent emission from porous silicon as a function of excitation energy support the conclusions of Kanemitsu et al.,66 Prokes and Glembocki,52 and Macauley et al.⁶⁷ The combination of these studies demonstrates that no obvious relationship exists between the PL spectrum and either the PLE spectrum or the particle size distribution. Kanemitsu et al., in examining the relationship between particle size and PL peak energy, have used optical absorption, Raman spectroscopy, and transmission electron microscopy to assess the relation between particle size and photoluminescence. They find a blueshift in the optical absorption spectrum for particles decreasing in size from 9 to 2 nm but observe no change in the corresponding PL peak energy. This result conclusively demonstrates that the PL peak emission energy is not correlated with the particle size. The data which we record in Fig. 2 over the $0-100 \ \mu s$ time frame also suggest the manifestation of a pumping sequence between a ground state and a strongly shifted excited state. The pumped excited-state levels, high in the excited-state manifold (Fig. 3), undergo nonradiative relaxation. This cascade process leads to a redshifting of the PL emission spectra as a function of increasing time following optical excitation^{3,57} suggesting, as we have noted, that the emission observed over a $0-100 \ \mu s$ time gate does not represent that from the lowest vibrational-rotational levels. With this caveat, we also note that the behavior of the PL in air is quite similar regardless of the manner in which a sample is properly prepared.³ These studies, in concert with the work of Prokes *et al.*^{2,52} and Macauley *et al.*,⁶⁷ strongly argue against quantum confinement as a source of the PS photoluminescence.

A number of researchers have recorded a blueshift in the PS photoluminescent emission spectrum which appears to parallel increasing etch effectiveness. While this blueshift has been attributed to the creation of quantum confined silicon particulates which decrease in size with increasing etch TABLE VI. Vibrational frequencies (cm⁻¹) and infrared intensities (km/mol) calculated for select silanone ground electronic states.

sym	ν	Ι	u	Ι		
	DZP	/MP2	DFT/TZVP			
Si(O)H(OSiH ₃)					Assignment	
<i>a'</i>	2408	78	2197	30	Si(O)-H str	
	2375	127	2185	59	SiH ₃ str	
	2362	68	2171	40	SiH ₃ str	
	1247	197	1245	185	Si=O str (dominant)	
	1073	57	1036	287	Si-O+SiH ₃ -O asym str	
	1018	652	904	262	SiH ₃ bend	
	1011	89	893	28	SiH ₃ bend	
	905	195	782	69	H-Si=O bend	
	753	58	697	34	SiH ₃ rock	
	602	2	613	6	SiH ₃ -O str	
	382	54	358	48	OSi=O bend	
	79	8	31	10	SiH ₃ -O-Si bend	
<i>a</i> ″	2367	133	2166	65	SiH ₃ str	
	1014	102	907	42	SiH ₃ bend	
	748	64	671	33	SiH ₃ rock	
	589	55	495	40	H-Si(O) out of plane	
	150	12	85	8	H-Si(Si=O+Si-O) out of plane	
	53	0.8			SiH ₃ torsion	
Si(O)(OH)(SiH ₂)						
a'	3903	124	3670	117	O-H str	
-	2365	71	2190	25	SiH ₂ str	
	2337	51	2162	19	SiH ₂ str	
	1222	85	1224	117	Si=0 str	
	986	56	904	44	Si-O str+SiH ₂ bend+H-O-Si bend	
	938	96	894	10	Si-O str + SiH ₂ bend + H-O-Si bend	
	886	241	826	168	SiH_2 bend+H-O-Si bend	
	836	219	810	198	SiH₂ bend−H-O-Si bend	
	563	21	525	11	SiH ₂ rock	
	458	28	432	33	Si-Si str+SiH ₂ bend+O-Si $=$ O bend	
	274	62	269	53	Si-Si str $-O$ -Si $=O$ bend	
	148	2	154	0.7	Si-Si=O bend	
<i>a</i> "	2350	74	2161	29	SiH ₂ str	
	987	55	907	17	SiH ₃ bend	
	550	18	510	2	SiH ₂ rock	
	487	172	449	172	H-O out of plane	
	240	10	240	5	$O.O.SiH_2$ out of plane	
	35	0.3	85	0.1	SiH ₂ torsion	
		0.0		÷		

^aCalculations performed at both the MP2 level with a polarized double-zeta basis set and using a triple-zeta valence basis set at the DFT level (Ref. 22).

time, one might also attribute the observed changes to the role of surface curvature (tension) and structural strain as it influences the PL process by creating local force gradients. In fact, Unagami⁶⁸ has measured the intrinsic stress in porous silicon layers formed in aqueous HF etch, finding a macroscopic stress which extends from compressive to tensile. Friedersdorf *et al.*⁶⁹ have observed the influence of stress on the PL of PS structures, correlating the blueshift in PL peak energy with surface microstructure. These authors conclude that the characteristic cellular structure occuring in high porosity films is due to high surface stresses. This cellular structure is not formed during the etching process itself but occurs during electrolyte evaporation after removal of the PS

from solution. Enhanced surface tensions associated with increased curvature appear to be operative. Finally, in close agreement, Kanecko, French, and Wolffenbuttel⁷⁰ have very recently noted that, while an enhanced etching cycle leads to a blueshift in the PL spectrum, the higher porosity structure created is clearly strained. While these authors note that the observed blueshift suggests quantum effects, the surface state of the porous layer also is suggested to play an important role.

The replicates of phonon structure that have been reported for PS samples at 2 K by Canham and co-workers^{4–6} and most recently by Collins, Fauchet, and Tischler⁷¹ are certainly intriguing and may indicate the signature for bulklike

silicon crystallites existent on a PS surface at low temperatures. Only Suemoto et al.⁷² have observed any semblance of this structure at temperatures exceeding 6 K (dependence of absorption edge structure at 78 K). However, the direct correlation of the suggested phonon structure observed at 2 K with the absorption edge recorded by several workers^{66,72} and the photoluminescence which dominates the emission from PS at room temperature is tenuous. Further, it is worth noting that alternate explanations might be invoked to explain what appear to be features similar to the transverse-optical⁶⁵ and transverse acoustical (Ref. 66) mode structure of bulk silicon. This structure, of course, is measured on the basis of energy shifts from an exciting laser frequency adjusted by the so-called exchange coupling factor Δ ,^{4–6} which increases with excitation frequency.⁵⁰ This invokes some concern as Δ varies approximately from 10 meV $(\sim 80 \text{ cm}^{-1})$ at 1.72 eV to 30.4 meV $(\sim 240 \text{ cm}^{-1})$ at 2.1 eV.^{5,50} This, of course, introduces a clear uncertainty into the measure of the frequency shifts from an exciting laser line as well as the meaning of onsets. However, even if we accept the application of this correction factor to the PLE spectra generated at 2 K, we are intrigued by the near matchup of the relevant silanone frequencies indicated in Table VI and the frequency separations for the broad phononlike features recorded by Calcott et al.5 Specifically, the anticipated Si-Si=O bending frequency given in Table VI, $\sim 150 \text{ cm}^{-1}$, is very close to the transverse-acoustical phonon frequency of bulk silicon. The silicon-silicon stretch fre-

- ¹L. T. Canham, Appl. Phys. Lett. 57, 1046 (1990).
- ²S. M. Prokes, J. Mater. Res. **11**, 305 (1996).
- ³F. Dudel, J. L. Gole, M. Reiger, and L. Bottomley (unpublished).
- ⁴See, for example, P. D. J. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, and D. Brumhead, J. Phys., Condens. Matter. 5, L91 (1993).
- ⁵P. D. J. Calcott, K. J. Nash, T. Canham, M. J. Kane, and D. Brumhead, J. Lumin. **57**, 257 (1993).
- ⁶K. J. Nash, P. D. J. Calcott, L. T. Canham, and R. J. Needs, Phys. Rev. B **51**, 17 698 (1995).
- ⁷A. Bsiesy, J. C. Vial, F. Gaspard, R. Herino, M. Ligeon, F. Muller, R. Romestein, A. Wasiela, A. Halimaoui, and G. Bomchil, Surf. Sci. **254**, 195 (1991).
- ⁸F. Dudel, J. L. Gole, M. Reiger, P. Kohl, J. Pickering, and L. Bottomley, J. Electrochem. Soc. **143**, L164 (1996).
- ⁹Y. H. Xie, W. L. Wilson, F. M. Ross, J. A. Mucha, E. A. Fitzgerald, J. M. Macauley, and T. D. Harris, J. Appl. Phys. **71**, 2403 (1992).
- ¹⁰F. Koch, V. Petrova-Koch, T. Muschik, A. Nikolov, and V. Gavrilenko, in *Microcrystalline Semiconductors: Materials Science & Devices*, edited by P. U. Fauchet *et al.* MRS, Proceedings No. 283 (Materials Research Society, Pittsburgh, 1993), p. 197; F. Koch, V. Petrova-Koch and T. Muschik, J. Lumin. 57, 271 (1993); F. Koch, in *Silicon-Based-Optoelectronic Materials*, edited by M. A. Tischler *et al.*, MRS Symposia Proceedings No. 298 (Materials Research Society, Pittsburgh, 1993), p. 222.
- ¹¹S. Prokes, O. J. Glembocki, V. M. Bermudez, R. Kaplan, L. E. Friedersdorf, and P. C. Pearson, Phys. Rev. B 45, 13 788 (1992);
 S. M. Prokes, J. Appl. Phys. 73, 407 (1993).

quency is of the order 450 cm^{-1} for the ground state of Si(O)(OH)(SiH₃) (Table VI) changing little for the excitedstate triplet (Table V). Not surprising is the close agreement between this frequency and that of the transverse-optical (~511 cm⁻¹) phonon mode frequency of a bulk silicon crystallite. Note also that the small change in the Si-Si bond distance is consistent with the observation by Canham and co-workers.⁴⁻⁶ of only two "phonon satellites" in their photoluminescence emission spectra at 2 K. This structure might simply be ascribed to a short progression in a ground-state Si-Si stretch, thus rendering the arguments presented by Calcott *et al.*⁴ concerning momentum conserving phonons tenuous. The observed phonon replicates clearly require considerable further study and correlation.⁷³

ACKNOWLEDGMENTS

We acknowledge very helpful discussions with Dr. Sharka Prokes and thank Professor Martin Stutzmann for providing us with data on his ODMR experiments. We also acknowledge financial support from the Office of the President at Georgia Institute of Technology under the auspices of the Focused Research Program. The quantum chemical calculations were performed under the auspices of the Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC06-76RLO 1830 with Battelle Memorial Institute, which operates the Pacific Northwest Laboratory.

- ¹²H. D. Fuchs, M. Rosenbauer, M. S. Brandt, S. Ernst, S. Finkbeiner, M. Stutzmann, K. Syassen, J. Weber, H. J. Queisser, and M. Cardona, in *Microcrystalline Semiconductors: Materials Science & Devices* (Ref. 10), p. 203.
- ¹³M. Stutzmann, M. S. Brandt, M. Rosenbauer, H. D. Fuchs, S. Finkbeiner, J. Weber, and P. Deak, J. Lumin. **57**, 321 (1993).
- ¹⁴M. S. Brandt and M. Stutzmann, Solid State Commun. 93, 473 (1995).
- ¹⁵A. J. Steckl, J. Xu, H. C. Mogul, and S. M. Prokes, J. Electrochem. Soc. **142**, L69 (1995).
- ¹⁶J. Yan, S. Shih, K. H. Jung, D. L. Kwong, M. Kovar, J. M. White, B. E. Gnade, and L. Magel, Appl. Phys. Lett. **64**, 1374 (1994).
- ¹⁷V. M. Dubin, F. Ozanam, and J. N. Chazalveil, Thin Solid Films 255, 87 (1995).
- ¹⁸F. P. Dudel, and J. L. Gole (unpublished).
- ¹⁹J. L. Gole, and D. A. Dixon (unpublished).
- ²⁰See, for example, L. E. Brus, P. F. Szajowski, W. L. Wilson, T. D. Harris, and P. H. Citrin, J. Am. Chem. Soc. **117**, 2915 (1995).
- ²¹M. S. Hybertsen, in *Light Emission from Silicon*, edited by S. S. Iyer, R. T. Collins, L. T. Canham MRS Symposia Proceedings No. 256 (Materials Research Society, Pittsburgh 1992), p. 179.
- ²²R. A. Street, Adv. Phys. 25, 397 (1976), and references therein.
- ²³See, for example, discussions in E. K. Propst and P. A. Kohl J. Electrochem. Soc. **141**, 1006 (1994).
- ²⁴ V. Lehmann, J. Electrochem. Soc. **140**, 2836 (1993); V. Lehmann and H. Fell, *ibid.* J. Electrochem. Soc. **137**, 653 (1990).
- ²⁵E. S. Astrova, S. V. Belov, A. A. Lebedev, A. D. Remenjuk, and Y. V. Rud, Thin Solid Films **255**, 196 (1995).
- ²⁶J. L. Gole and D. A. Dixon (unpublished).

- ²⁷H. Gerischer, P. Allongue, and V. C. Kieling, Ber. Bunsenges. Phys. Chem. **97**, 753 (1993).
- ²⁸V. Lehmann and U. Gosele, Appl. Phys. Lett. 58, 856 (1991).
- ²⁹G. W. Trucks, K. Raghavachari, G. H. Higashi, and Y. J. Chabal, Phys. Rev. Lett. **65**, 504 (1990).
- ³⁰The evaluation of the radiative lifetime for the green emitting precursor state can be complicated both by its continual formation during the radiative decay process and by its chemical transformation during the course of an emission decay measurement.
- ³¹R. J. Glinski, J. L. Gole, and D. A. Dixon, J. Am. Chem. Soc. 107, 5891 (1985).
- ³²D. A. Dixon and J. L. Gole, Chem. Phys. Lett. **125**, 179 (1986).
- ³³J. Andzelm, E. Wimmer, and D. R. Salahub, in *The Challenge of d and f Electrons: Theory and Computation*, edited by D. R. Salahub, and M. C. Zerner, ACS Symposia Series No. 394 (American Chemical Society, Washington, D.C., 1989), p. 228; J. Andezelm, in *Density Functional Theory in Chemistry*, edited by J. Labanowski and J. Andzelm (Springer-Verlag, New York, 1991), p. 155; J. W. Andzelm and E. Wimmer, J. Chem. Phys. **96**, 1280 (1992).
- ³⁴ M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Closlowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople, GAUSSIAN 94, Revision B.2 (Gaussian, Inc., Pittsburgh, PA, 1995).
- ³⁵S. M. Prokes, J. Electrochem. Soc. Interface, Summer, 41 (1994).
- ³⁶N. Godbout, D. R. Salahub, J. Andzelm, and E. Wimmer, Can. J. Chem. **70**, 560 (1992).
- ³⁷A. Komornicki and G. Fitzgerald, J. Chem. Phys. **98**, 1398 (1993), and references therein.
- ³⁸C. Moller and M. S. Plesset, Phys. Rev. **46**, 618 (1934); J. A. Pople, J. S. Binkely, and R. Seeger, Int. J. Quantum Chem. Symp. **10**, 1 (1976).
- ³⁹T. H. Dunning, Jr. and P. J. Hay, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), Chap. 1; A. D. McLean and G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980).
- ⁴⁰ R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989); S. A. Kucharski and R. J. Bartlett, Adv. Quantum Chem. **18**, 281 (1986); R. J. Bartlett and J. F. Stanton, in *Reviews of Computational Chemistry, Vol. V*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1995), Chap. 2, p. 65.
- ⁴¹For the Si basis, see K. D. Dobbs and D. A. Dixon, J. Phys. Chem. **98**, 5290 (1994); for O and H, see K. D. Dobbs, D. A. Dixon, and A. Kormonicki, *ibid.* **98**, 8852 (1993).
- ⁴²See, for example, G. J. Green and J. L. Gole, Chem. Phys. **100**, 133 (1985).
- ⁴³See also M. S. Brandt, and M. Stutzmann, Appl. Phys. Lett. **61**, 2569 (1992); M. Stutzmann, J. Weber, M. S. Brandt, H. D. Fuchs, M. Rosenbauer, P. Deak, A. Hopner, and A. Breitschwerdt, Festköerperprobleme **32**, 179 (1992); M. Stutzmann, M. S. Brandt, E. Bustarret, H. D. Fuchs, M. Rosenbauer, A. Hopner, and J. Weber, J. Non-Cryst. Solids **164–166**, 931 (1993); M. Rosenbauer, M. S. Brandt, H. D. Fuchs, A. Hopner, A. Breitschwerdt, and M. Stutzmann, in *Optical Properties of Low Dimensional Silicon Structures*, Vol. 244 of *NATO Ad*-

vanced Study Institute, Series E: Applied Sciences, edited by D. C. Bensahel, L. T. Canham, and S. Ossicini (Kluwer, Dordrecht, 1993), p. 43; M. S. Brandt, M. Rosenbauer, and M. Stutzmann, in *Silicon-Based Optoelectronic Materials* (Ref. 10, p. 301).

- ⁴⁴J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, England, 1961); B. C. Cavenett, Adv. Phys. **30**, 475 (1981); K. M. Lee, L. C. Kimerling, B. G. Bagley, and W. E. Quinn, Solid State Commun. **57**, 615 (1986).
- ⁴⁵H. D. Fuchs, M. Stutzmann, M. S. Brandt, M. Rosenbauer, J. Weber, A. Breitschwerdt, P. Deak, and M. Cardona, Phys. Rev. B 48, 8172 (1993).
- ⁴⁶ M. Zacharias, D. Dimova-Malinovska, and M. Stutzmann, Philos. Mag. B **73**, 799 (1996).
- ⁴⁷A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970); A. M. Stoneham, *Theory of Defects in Solids* (Clarendon, Oxford, 1975), Chap. 13 and Appendix II.
- ⁴⁸This is the ODMR powder pattern. See R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge, England, 1991), p. 106.
- ⁴⁹M. Stutzmann (private communication).
- ⁵⁰Calcott *et al.* (Refs. 4 and 5) suggest that, to reasonable approximation, $\Delta \propto (h\omega_p E_{gap})^{1.5}$ where $E_{gap} = 1.17 \text{ eV}$ is the 2-K band-gap energy of bulk silicon and a calculation at $h\omega_p = 1.72 \text{ eV}$ fixes the constant of proportionality. At 2.1 eV, this gives (const=33.9) $\Delta = 30.4 \text{ meV}$, at 3.5 eV, the peak of the PLE spectrum, we find $\Delta = 121 \text{ meV}$. The implied Δ at room temperature would increase slightly to 125 meV if the constant of proportionality holds over the range 2–300 K).
- ⁵¹Neglecting the electron-hole interaction and effective mass theory (see Ref. 4.)
- ⁵²S. M. Prokes and O. J. Glembocki, Phys. Rev. B 49, 2238 (1994);
 S. M. Prokes, W. E. Carlos, and O. J. Glembocki, *ibid.* 50, 17 093 (1994); W. E. Carlos and S. M. Prokes, J. Appl. Phys. 78, 2127 (1995); 78, 2129 (1995); S. M. Prokes and W. E. Carlos, *ibid.* 78, 2671 (1995).
- ⁵³Anton Fojtik and Arnim Henglein, Chem. Phys. Lett. 221, 363 (1994).
- ⁵⁴A. Fojtik, M. Giersig, and A. Henglein, Ber. Bunsenges. Phys. Chem. 97, 1493 (1993).
- ⁵⁵M. S. Hybertsen, in *Light Emission from Silicon* (Ref. 21), p. 179.
- 56 The excitation source for these time-resolved emission studies was a 500-Hz Nd:YAG regenerative amplifier seeded with an Antares cw mode-locked Nd:YAG laser. The 65-ps, 1.064- μ m output was tripled to generate 355-nm pulses.
- ⁵⁷R. Laiho, A. Pavlov, and T. Tsuboi, J. Lumin. **57**, 89 (1993).
- ⁵⁸ V. M. Dubin, F. Ozanam, and J. N. Chazalviel, Thin Solid Films 255, 87 (1995).
- ⁵⁹ M. A. Hory, R. Herino, M. Ligeon, F. Muller, F. Gaspard, I. Mihalcesu, and J. C. Vial, Thin Solid Films **255**, 200 (1995).
- ⁶⁰ M. Zacharias, D. Dimova-Malinovska, and M. Stutzmann, Philos. Mag. B 73, 799 (1996).
- ⁶¹See also the matrix infrared study of R. Withnall and L. Andrews, J. Phys. Chem. **89**, 3261 (1985).
- ⁶²F. P. Dudel, D. Grantier, and J. L. Gole (unpublished).
- ⁶³James L. Gole and Frank P. Dudel, J. Appl. Phys. (to be published).
- ⁶⁴ J. Rolfe, J. Chem. Phys. **40**, 1664 (1964); J. Rolfe, F. R. Lipsett, and W. J. King, Phys. Rev. **123**, 447 (1961).
- ⁶⁵P. J. Dean, J. R. Haynes, and W. F. Flood, Phys. Rev. **161**, 711 (1969); K. L. Shaklee and R. E. Nahory, Phys. Rev. Lett. **24**,

942 (1970); T. Nishino, M. Takeda, and Y. Hamakawa, Solid State Commun. 14, 627 (1974).

- ⁶⁶Y. Kanemitsu, H. Uto, Y. Matsumoto, T. Futagi, and H. Mimura, Phys. Rev. B **48**, 2827 (1993); Y. Kanemitsu, T. Matsumoto, T. Futagi, and H. Mimura, Jpn. J. Appl. Phys. 1 **32**, 411 (1993).
- ⁶⁷J. M. Macauley, F. M. Ross, P. C. Searson, S. K. Sputz, R. People, and L. E. Friedersdorf, in *Light Emission from Silicon* (Ref. 21), p. 47.
- ⁶⁸T. Unagami, J. Electrochem. Soc. 144, 1835 (1997).

- ⁶⁹L. E. Friedersdorf, P. C. Searson, S. M. Prokes, O. J. Glembocki, and J. M. Macaulay, Appl. Phys. Lett. **60**, 2285 (1992).
- ⁷⁰H. Kanecko, P. J. French, and R. F. Wolffenbuttel, J. Lumin. 57, 101 (1993).
- ⁷¹R. T. Collins, P. M. Fauchet, and M. A. Tischler, Phys. Today **50** (1), 24 (1997).
- ⁷² T. Suemoto, K. Tanaka, A. Nakajima, and T. Itakura, Phys. Rev. Lett. **70**, 3659 (1993).
- ⁷³James L. Gole, D. A. Dixon, and S. Prokes (unpublished).