Journal of
Applied Physics

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Cite as: Journal of Applied Physics **83**, 5985 (1998); https://doi.org/10.1063/1.367464
Submitted: 22 December 1997 . Accepted: 06 March 1998 . Published Online: 13 October 1998

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JOURNAL OF APPLIED PHYSICS VOLUME 83, NUMBER 11 1 JUNE 1998

Evidence for oxide formation from the single and multiphoton excitation of a porous silicon surface or silicon ''nanoparticles''

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(Received 22 December 1997; accepted for publication 6 March 1998)

Potential oxidation as monitored by single and multiphoton excitation and associated with the laser induced photoluminescence (PL) from silicon nanoparticles and a porous silicon (PS) surface is considered in the light of recent *in situ* observations of the photoluminescence process coupled with detailed quantum chemical modeling of the silanone based oxyhydrides. The enhanced oxidation of PS surface bound SiH_x moieties as they undergo multiphoton excitation through the SiH_x stretch vibrational ladder to the quasicontinuum is suggested as a source of the visible PL produced in the 600–800 nm region. Vibrational-to-electronic energy transfer within the SiH_x manifold, as previously suggested, is thought to be unlikely. However, the formation of $OSiH_x$ constituencies on the PS surface as these are associated with the silanone-based silicon oxyhydrides would appear to be significant. Evidence for these oxyhydrides may also be apparent in the laser induced PL from silicon nanoparticles. All experimental observations are explained without envoking quantum confinement. © *1998 American Institute of Physics.* [S0021-8979(98)08211-5]

I. INTRODUCTION

The discovery of room temperature visible luminescence[1] 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. While the luminescence is thought to occur near the silicon surface,[2,3] the source of the luminescence is controversial as the efficiency and wavelength range of the emitted light can be affected by the physical and electronic structure of the surface and the nature of the etching solution.[4,5] Recently, Wang *et al.*[6] have carried out an enticing experiment in which they produce the characteristic luminescence band extending from 550 to 650 nm using the 1.064 μm output from a Nd-yttrium aluminum garnet (YAG) laser, finding a luminescence output proportional to I_{in}.[3] These authors have suggested a third harmonic excitation in the core of silicon crystallites. Even more intriguing have been the elegant infrared multiphoton excitation (MPE) experiments of Chin, Shen, and Petrova–Koch,[7] who have obtained the characteristic orange-red photoluminescence using infrared multiphoton (4.9 μm) excitation primarily in the region of the SiH_x stretch frequencies. While the use of 1.064 μm radiation might result in a direct MPE of carriers into the ''Urbach tail'' region,[6] Chin *et al.*[7] have noted that the luminescence induced via MPE through a vibrational manifold strongly suggests that surface species on the PS must also be involved in the process. Recent experiments[8] and detailed quantum chemical modeling[9] conducted in our laboratories provide information which now suggests an alternate interpretation of these important MPE experiments. We will associate the visible photoluminescence (PL) from the (MPL) experiments and from the laser induced pumping of silicon nanocrystals with the oxidation of a silicon hydride moiety on the PS or nanocrystal surface.[10]

We have carried out an extensive series of experiments[5,8] in both aqueous (HF/H_2O,$HF/CH_3OH/H_2O$,$HF/C_2H_5OH/H_2O$,$HF/H_2O/HCl$) 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.[5,8] These experiments 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(a)] 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.[8(e)] This result, which is not consistent with quantum confinement,[11] suggests the pumping of the excited state manifold of a molecule-like species followed by rapid nonradiative relaxation through the manifold and the subsequent emission of radiation at a much longer wavelength.

The experiments are supported by detailed quantum chemical modeling[9] which suggests a close correlation with the manifold of electronic states associated with the silanone based silicon oxyhydrides of the form $O{=}\ddot{Si}{-}OH$[12] or

$O=\ddot{S}i-OSiH_3$. Changes in bonding associated with electronic transitions involving the oxyhydride ground electronic and low-lying triplet states,[13] 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 red shift of the PL spectrum (600–800 nm) from the known absorption peak wavelength of the (PLE) excitation spectrum (~350 nm).[10]

II. CORRELATION OF EXPERIMENTAL RESULTS AND QUANTUM CHEMICAL MODELING—MULTIPHOTON EXCITATION

Wang *et al.*[6] have prepared PS samples in a manner which would appear to produce not only the precursor of the well known orange-red emission feature but also some component of the constituency which produces a green photoluminescence from the PS surface.[8(c)] This probably results from their ~1 s dip in HF.[8(c)] These authors observe a luminescence output proportional to the third power of the 1.064 μm line of a Nd:YAG laser which they attribute to a single third harmonic photon.

Chin *et al.*,[7] in studying the photoluminescence induced by infrared multiphoton excitation, prepared their PS layers through the anodic etching of (100) *p*-type crystalline silicon wafers followed by aging in air. These samples, left in air for extended periods, displayed Fourier transform infrared (FTIR) spectra for SiH_x, SiO_x, and $OSiH_x$ species coexisting on the PS surface.[14] Chin *et al.* irradiated these extensively air aged surfaces[15] in air at power densities between 1 and 3 GW/cm^2, finding no degradation of PL or damage to the samples under this irradiation. However, it is to be noted that these power densities do provide a means of removing at least the first several monolayers of the PS surface. This cleaning, coupled with the short time scale necessary to generate PL emitters on the surface,[8(a),(e)] suggests the formation of freshly formed PL emitters at the surface. The PL spectrum obtained with a 4.9 μm MPE pump, and measured with a time delay from 100 ns to 100 μs, is displayed in Fig. 1 where it is compared[7] with spectra excited using 0.532, 1.064, and 1.3 μm radiation. As Chin *et al.* have noted, the emission of a single photon at 700 nm requires the absorption of *at least* one, two, two, and seven photons at 0.532, 1.06, 1.3, and 4.9 μm (2060 cm^{-1}). From their data as reproduced in Fig. 1, it is clear that very similar PL spectra are produced, independent of excitation wavelength.

Chin *et al.*[7] find an $I_{\mathrm{in}}{}^5$ dependence of the PL output on the input intensity at 4.9 μm. These authors scanned their pulsed infrared radiation source over the SiH_x and $OSiH_x$ vibrational resonances in the region ranging from 1900 to 2280 cm^{-1} to generate the data depicted in Fig. 2. The vibrational absorption spectrum of a sample, left in air for an extended period both before and during the measurement, exhibits a broad band centered at ~2120 cm^{-1} which is assigned to SiH_x, and a second sharper feature centered at 2260 cm^{-1} which has been identified with $OSiH_x$. Chin *et al.* suggest that the MPE process is effective only when it occurs via the vibrational ladder of SiH_x and cannot be connected with the formation of the $OSiH_x$ manifold of states. However, we will suggest that their data, as depicted in Fig. 2, bears reconsideration. Not only the frequencies associated with the SiH_x moieties but also and especially the O_xSiH and $OSiH_x$ group frequencies are expected to vary with (1) adjacent atom and surface environment and (2) specific hydrogen and oxygen bonding. The O_xSiH band (Si–H stretches) is known to extend over the 2150–2300 cm^{-1} region,[16] dependent on the conditions of its formation. Although the lower excitation MPE-PL spectrum appears to display a correlation only with the SiH_x spectral feature, as the intensity increases, two clear peaks both shifted significantly to lower frequencies (~2040 and ~2200 cm^{-1}) from the SiH_x and $OSiH_x$ vibrational absorptions are apparent. Chin *et al.* suggest that,

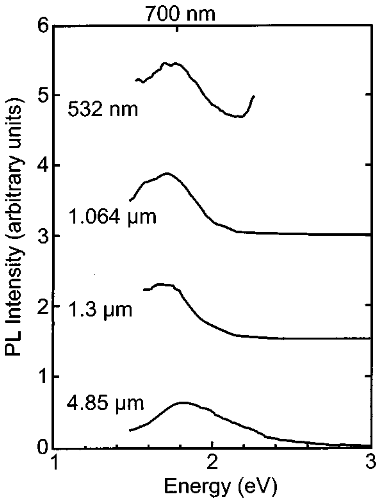


FIG. 1. The visible orange-red photoluminescence from porous silicon excited by 0.532, 1.064, 1.3, and 4.9 μm multiple photon absorption. (From Ref. 7.)

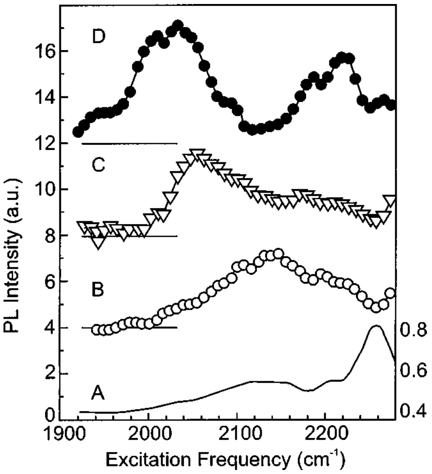


FIG. 2. (a) The vibrational absorption spectrum of a porous silicon sample showing a broad feature at ~2120 cm^{-1} due to $-SiH_x$ moieties and a sharper absorption at ~2260 cm^{-1} due to $OSiH_x$ moieties and (b)–(d) MPE-PL excitation spectra in the $-SiH_x$ and $-OSiH_x$ stretch vibrational frequency range for infrared pump intensities of (b) 0.4, (c) 0.8, and (d) 2.8 GW/cm^2. (From Ref. 7.)

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

Molecule	r(Si═O)	r(Si═O)	Δr(Si═O)
	singlet	triplet	
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)SiH_3(OH)	1.543	1.712	0.169
Si(O)$(SiH_3)_2$	1.560	1.681	0.121
Si(O)SiH_3($OSiH_3$)	1.543	1.712	0.169

[a] Bond length for the excited singlet is 1.705 Å. See the text for discussion.
[b] Bond lengths for HO–Si–OH silylene are 1.670 Å for the ground state singlet and 1.680 Å for the excited triplet.

TABLE II. Ground state singlet—excited triplet energy separation for silanones (silylenes).

Molecule	$\Delta E(S-T)$	$\Delta E(S-T)$	$\sim\lambda_{\text{Adiabatic}}$ (nm)
	kcal/mol	eV	
Si(O)H_2	61.1	2.65	475
Si(O)H(OH)	70.9	3.07	403
Si(O)$(OH)_2$	71	3.08	402
Si(0)H($OSiH_3$)	70.3	3.05	406
Si(O)SiH_3(OH)	71.2	3.09	401
Si(O)H(SiH_3)	57.3	2.48	499
Si(O)SiH_3($OSiH_3$)	69.6	3.02	411
Si(O)$(SiH_3)_2$	53.9	2.34	530
HSiOH	38.4	1.66	744
HOSiOH	64.2	2.78	445
SiH_3OSiOH	63.4	2.75	425

in fact, the broad excitation peak characteristic of SiH_x simply splits into two; however, the splitting and shift of the higher energy component certainly appears to be much more pronounced suggesting instead its correlation with a significant oxygen backboning to the SiH_x group. We therefore will suggest that the 2200 cm^{-1} feature should be correlated with an intermediate $OSiH_x$ constituency, displaying the anticipated effect of anharmonicity, and not SiH_x. We will also consider further evidence for oxidation to form the $OSiH_x$ moiety as indicated by single photon laser induced PL experiments.

III. QUANTUM CHEMICAL MODELING—THE NATURE 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 study[9] of several model compounds. We have employed *ab initio* molecular orbital theory using the program GAUSSIAN 94.[17] The molecules Si(O)H_2, Si(O)H(OH), Si(O)$(OH)_2$, Si(O)H($OSiH_3$), Si(O)H(SiH_3), Si(O)(OH)(SiH_3), Si(O)$(SiH_3)_2$, and Si(O)SiH_3($OSiH_3$) were used as models for the various sites that might be present on a hydrogen-passivated silicon surface[18] 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.

Geometries were optimized at the (MP2)/(DZP) level[19,20] 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)H_2 at the optimized geometries. These calculations were done at the (CCSD(T)) level[21] with a triple zeta basis set[22] augmented by two sets of polarization functions on all atoms and by f functions on the heavy atoms.

The most relevant results of these calculations are summarized in Tables I–III. A detailed description of the calculations is given elsewhere.[9] In Table I we summarize the Si=O bond lengths determined for the ground state singlet and low-lying 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 SiO bonds. The data in Table II indicates that the calculated singlet-triplet separations for the model silanone compounds containing an OH or $OSiH_3$ group are consistent with the porous silicon PLE spectrum.

It is noteworthy that the locations of the unsaturated silicon oxyhydride excited triplet states with OH or $OSiH_3$ moieties and the known peak wavelength of the (PLE) excitation spectrum ($\sim$350 nm)[10] both bear a clear resemblance to the known singlet-triplet splittings of the low-lying silicon monoxide intercombination band systems[23] which occur in the same energy region. The large change in the SiO bond lengths indicated in Table I in turn produces a large shift in the excited triplet state potential relative to the ground state, consistent with a significant difference in the peak of the PLE excitation spectrum ($\sim$350 nm) and the observed PL emission range [$\sim$500–550 nm (green), $\sim$600–800 nm (orange)]. Changes in the remaining-silanone bonds upon optical excitation are at least an order of magnitude smaller.[8,9] The data is also consistent with efficient excitation pumping high up the excited state triplet manifold, at wavelengths considerably shorter than 400 nm,[9] followed by subsequent relaxation within the excited state manifold before emission (Fig. 3).

Although the peak in the PL excitation spectrum occurs at $\sim$350 nm, the data presented in Fig. 4 have been obtained with a KrF excimer laser pump at 248 nm. The emission range is typical of the PL obtained from [similarly prepared PS] pumped across a wide range of laser wavelengths.[8(e)] However, here the PS surface has been prepared in a *nonaqueous* etching solution[5,8] [MeCN/HF (2 M) @$H_2O \leqslant 0.001$ Mol/l]. Upon removal from the etching solution, rinsing in methanol and drying in air, we observe that an initially weak orange-red PL increases significantly with time. The influence of the oxidation process in air is apparent. Further studies suggest that the predominant oxidizing agent is H_2O[6,8(b)] followed by O_2 which may form an O_2^- intermediate on the surface.[8(d)]

There are additional striking trends which are associated with the data of Tables I and II. First, we note that whenever an OH or $OSiH_3$ (OR) group is bound to the silicon–oxygen bond, the change, Δr (SiO), is consistently of order 0.17 Å.

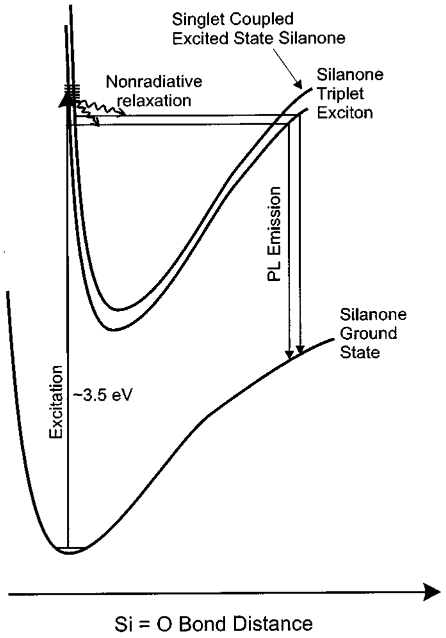


FIG. 3. Rough schematic of silicon oxyhydride ground state singlet and excited state triplet potentials indicating (1) the possible origin of the substantial difference in photoluminescence excitation (PLE) and subsequent photoluminescence (PL) emission energies.

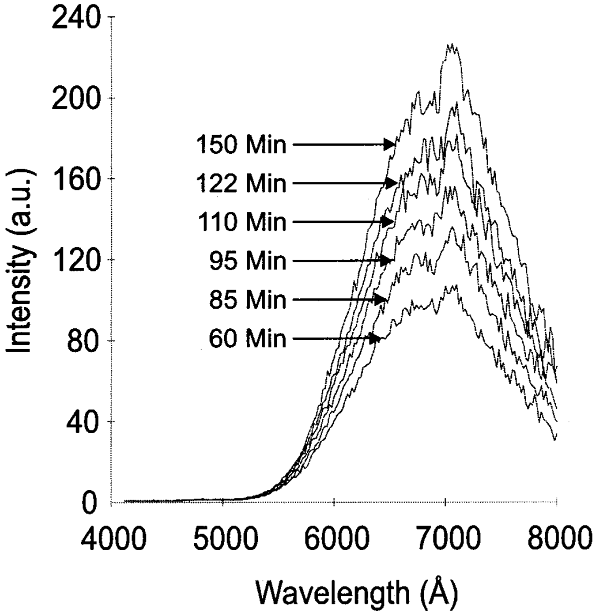


FIG. 4. PL spectra obtained with a KrF excimer laser in air as a function of time after a PS sample was etched in near anhydrous 2 M HF/MeCN for 10 min at 8 mA/cm^2, removed from the etch solution, rinsed in methanol, and dried in air. An initially weak orange-red PL increases significantly with time. Spectra are corrected for system response. The time gate for sampling was 0.8–100 μs.

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 $Si(O)H_2$ to 0.121 Å for $Si(O)(SiH_3)_2$. There 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 bond. Contrast these virtually identical energy increments to the much lower and decreasing adiabatic energy differences associated with the series $Si(O)H_2$ ($\Delta r = 0.155$ Å), $Si(O)H(SiH_3)$ ($\Delta r = 0.142$ Å), and $Si(O)(SiH_3)_2$ ($\Delta r = 0.121$ Å) where the smaller change, Δr (SiO), in the SiO bond length will lead to a smaller red shift of the PL emission feature. These results indicate that the oxyhydrides with bound –OR ligands will produce a larger red shift of the PL emission spectrum relative to the peak of the PLE excitation spectrum than those fluorophors having only R group ligand binding. In fact, we have argued that the magnitudes of these changes are relevant to the correlation of the mechanism for PS formation with the assignment of its transforming green and final orange-red photoluminescence emissions.[8(c)] We associate the green emitter with an R group bound fluorophor and the orange emitter with the oxidative insertion into an SiH (→SiOH) or Si–SiH_x ($SiOSiH_x$) bond.

The results which we obtain in the outlined calculations not only can be used to readily explain the character of the observed PL emission from a PS surface undergoing oxidation, but also they are consistent with the nature of the emission observed from silicon nanocrystals.[10] Brus *et al.*[10] have obtained the PL spectra depicted in Fig. 5 for ‘‘silicon

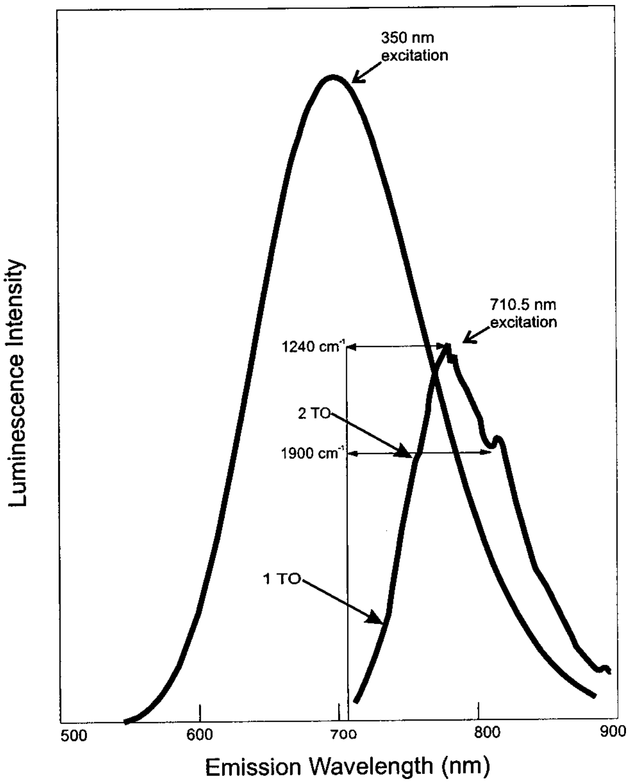
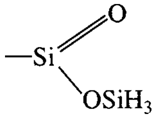


FIG. 5. Comparison between a 350 nm excited (low-resolution 3 nm) emission spectrum from Si nanocrystals at ~15 K and a high resolution (0.2 nm) emission spectrum excited at 710.5 nm. Relative intensities are arbitrary. The features labeled 1 TO and 2 TO in the 710.5 nm excitation spectrum correspond to extremely weak thresholds which have been correlated (Ref. 10) with the transverse optical phonon frequency of *c*-Si (data from Ref. 10).

nanocrystals'' pumped at 350 and 710.5 nm. The 350 nm pump spectrum taken at a resolution of 3 nm shows little structure and is similar to the spectra depicted in Fig. 4 and those observed by several other groups. The 710.5 nm excitation spectrum is intriguing in that it displays two clear peaks Stokes shifted from the 710.5 nm excitation by $\sim 1240 \pm 10$ and $1900 \pm 20\ \mathrm{cm}^{-1}$, respectively. These two peaks were not identified by Brus *et al.*[10] who chose to correlate the very weak thresholds shifted by ~475 and $904\ \mathrm{cm}^{-1}$ with 1TO and 2TO transverse optical frequencies in analog to *c*-Si. In view of the similar structure observed by Suemoto *et al.*[24] at a much higher 78 K temperature, which shows the clear separations indicative of a Si–Si stretch mode, the assignment of the threshold features in Fig. 4 at 15 K seems tenuous.[25] However, based on our quantum chemical modeling, we wish to suggest a plausible assignment for the two major peaks observed in the spectrum.

Calculated infrared spectral frequencies for $Si(O)SiH_3(OSiH_3)$ are given in Table III. Whereas the calculated values in this table are for the silanone based molecule, they provide an indication of the frequencies which should be associated with the surface bound fluorophor —Si(O)—$OSiH_3$. Most important for our considerations is the calculated Si═O stretch vibration at $\sim 1220\ \mathrm{cm}^{-1}$ and the (O)SiH_3 rock at $\sim 680\ \mathrm{cm}^{-1}$. These calculated frequencies suggest that the Si═O stretch mode and a combination band of the Si═O stretch and $OSiH_3$ rock for the silanone based oxyhydride fluorophor

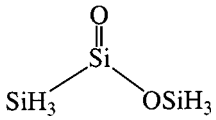


bound to the surface of the silicon nanocrystal might well account for the major features in the emission associated with the 710.5 nm excitation spectrum (Fig. 5) of Brus *et al.*[10] We suggest that this correlation certainly indicates the possibility of a significant oxyhydride surface coating of the nanocrystal.

We have also evaluated the possible contribution to the PS photoluminescence of surface bound tricoordinated silicon centers, SiXYZ, which possess a dangling electron. Excitations of the singly occupied electron or from fully occupied orbitals into the electrons singly occupied orbital might require sufficiently low energies so that emission from the resulting excited states can contribute to the observed spectral features. We have modeled this site with a silicon coordination ranging from SiH_3 to $Si(OH)_3$ with the progressive replacement of hydrogen by an OH ligand. Ground state geometries were again optimized and vibrational frequencies were calculated to demonstrate that the structures corresponded to minima.[26] Excited state energies were calculated at these minimum geometries using the configuration interaction singles [configuration interaction (CI) singles] method where the excited states are modeled as single excitations from the Hartree–Fock ground state.[27] Six states were determined using this CI-singles approach. We benchmarked the method with the molecule SiH_3 for which experimental data is available. The A–X transition for SiH_3 has been observed in the region 205–250 nm.[28] Energies were initially calculated with the augmented polarized triple zeta basis set used for studies of $Si(O)H_2$.[9] For SiH_3 the lowest transition energy is associated with a degenerate excitation at 204 nm (6.07 eV) located in the same region as the experimental spectrum. It is clear from the calculated and experimental results that a tricoordinated silicon with a dangling electron cannot account for either the excitation spectrum (PLE) or the features (PL) that are associated with the MPE visible emission depicted in Fig. 1.

TABLE III. Calculated frequencies ($\nu \geqslant 450\ \mathrm{cm}^{-1}$).[a,b]

for



$\nu(\mathrm{cm}^{-1})$	I(km/mol)	Assignment
2198	47	(SiH_3)–Si(Si–H) stretch
2186	88	(SiH_3)–O(Si–H) stretch
2178	85	(SiH_3)–O(Si–H) stretch
2177	71	(SiH_3)–O(Si–H) stretch
2172	53	(SiH_3)–Si(Si–H) stretch
2167	28	(SiH_3)–Si(Si–H) stretch
1220	175	Si═O stretch
1031	382	Si–O–Si asymmetric stretch
910	287	SiH_3O (inv) bend
898	34	SiH_3O (inv) bend
895	37	SiH_3O (inv) bend
892	28	SiH_3–Si bend
889	15	SiH_3–Si bend
803	253	SiH_3 (inv) bend
691	39	SiH_3(O) rock
677	39	SiH_3(O) rock
619	5	Si–O–Si symm. stretch
507	4	SiH_3(Si) wag
483	21	SiH_3(Si) wag
452	30	Si–Si stretch+Si–O–Si bend

[a] Frequency range of FTIR spectra exceeds $450\ \mathrm{cm}^{-1}$.

[b] Calculations at MP2/DZP level.

Predicted SiH_x harmonic frequencies for the ground state singlet and low-lying triplet state of several additional silanone based oxyhydrides are given in Table IV. These calculated frequencies should be scaled by ~0.95 to account for anharmonic effects. For our considerations, it is important to note that the SiH_x group frequencies, especially for the heavier silanones, change by a relatively small frequency increment as one undergoes a transition from the singlet ground state to the low-lying triplet state. This small change, which suggests that the portions of the potentials describing these modes for the singlet and triplet are very similar, *implies that the overlap of high vibrational levels in the ground state* SiH_x *manifold with the energetically isoergic levels in the triplet state will be small.*

IV. DISCUSSION

Within the generic model of infrared MPE, at sufficiently high beam intensities, it is possible to overcome the difficulties inherent to the excitation of off-resonant vibrational transitions which result from vibrational anharmonicity. Direct MPE of a molecule (or fluorophor) to the so-

TABLE IV. SiH_x vibrational frequencies (ν in cm^{-1}) and infrared intensities (I in km/mol) for the ground state and low-lying triplet states of the silanone based silicon oxyhydrides.[a]

sym	ν	I	ν	I	Approximate assignments
	singlet		triplet		
$Si(O)H_2$					
a_1	2345	53	2275(a')	23	Si–H sym str
b_1	2354	166	2311(a'')	102	Si–H asym str
Si(O)H(OH)					
a'	2419	72	2298(a)	106	Si–H str
$Si(O)H(SiH_3)$					
a'	2362	67	2346(a)	84	SiH_3 str
	2323	53	2337(a)	88	SiH_3 str
	2280	177	2267(a)	66	Si(O)–H str
a''	2332	81	2324(a)	87	SiH_3 str
$Si(O)(SiH_3)_2$					
a	2352	49	2345	72	$Si-H_3$ str
	2351	91	2344	87	$Si-H_3$ str
	2326	151	2336	164	$Si-H_3$ str
	2325	12	2334	0	$Si-H_3$ str
	2317	79	2323	71	$Si-H_3$ str
	2312	53	2319	75	$Si-H_3$ str
$Si(O)H(OSiH_3)$					
a'	2408	78	2263(a)	135	Si(O)–H str
	2375	127	2364(a)	133	SiH_3 str
	2362	68	2354(a)	117	SiH_3 str
a''	2367	133	2342(a)	123	SiH_3 str
$Si(O)(OH)(SiH_3)$					
a'	2365	71	2341(a)	86	SiH_3 str
	2337	51	2339(a)	86	SiH_3 str
a''	2350	74	2324(a)	64	SiH_3 str

[a] Calculated at the MP2/DZP level of theory (Ref. 9).

called quasicontinuum with its high density of levels can become significant. A molecule which has been excited to the quasicontinuum, can be readily pumped by single photon resonance steps until it reaches a level such that it can cross over to the electronically excited states which are energy resonant with the ground state vibrational manifold. The coupling to these states, of course, depends also on the overlap of the ground and excited state vibrational wave functions.

Chin *et al.*[7] envision PS as a series of weakly connected quantum sized clusters of silicon with each cluster terminated by SiH_x or $OSiH_x$ moieties. They note that the PS absorption spectrum around the band edge is affected by the quantum size effect and reason that a long Urbach tail in the spectrum results from transitions between band states and surface states. However, a direct correlation to the PL is not established. Chin *et al.* suggest that, while the luminescence (PL) can result from direct MPE of carriers into the Urbach tail region through the use of 1.06 and 1.3 μm radiation, the luminescence induced in their experiments with 4.9 μm infrared MPE excitation of vibrational resonances strongly suggests that surface species are involved in the process. We suggest that the outlined observations do not require the formation of quantum confined crystallites.

Kanemitsu *et al.*[29] have examined the relationship between particle size and photoluminescence peak energy using optical absorption, Raman spectroscopy, and transmission electron microscopy to assess the particle size and photoluminescence. They find a blue shift 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, in agreement with laser excitation experiments[8(c)] conclusively demonstrates that the PL peak emission energy is not correlated with particle size.

The process which is limited by the MPE step to the quasicontinuum appears to require five photons for the 4.9 μm excitation of the PL from PS,[7] suggesting the effective quasicontinuum begins at 1.25 eV. This, quantum chemistry and experiment demonstrate, is well below the energy required for a $V-E$ transfer in the SiH_x manifold. The required photon flux must correspond to at least an eight photon process and, as Tables III and IV suggest, *the ground and excited state silanone* SiH_x *manifolds also have a poor vibrational overlap*.

Even though the SiH_x stretch peaks are certainly inhomogeneously broadened at high pump power, their lifetimes must become shorter than the pump pulse width in order that they be effectively coupled with the other vibrational modes of the system to form the required ground state quasicontinuum. This seems difficult through the SiH_x manifold. However, an alternate association would appear to be possible as suggested by the width of the vibrational bands reproduced in Fig. 2. A polyatomic molecule or surface bound fluorophor in a high degree of vibrational excitation considerably expands its configuration space and reactivity.[30] This increased reactivity in the case of PS can readily be manifest by an enhancement of the oxidation process. If the two peaks observed in the high excitation energy MPE-PL spectrum, in fact, both correspond to red shifted SiH_x ($\sim 2040\ cm^{-1}$) and $OSiH_x$ ($\sim 2200\ cm^{-1}$) features associated with vibrational excitation, *then the onset of the* $OSiH_x$ *peak likely results from a highly efficient oxidative process involving the* SiH_x *manifold*. This, of course, can produce PL involving the $OSiH_x$ moiety. The exclusion of the $OSiH_3$ manifold or an O_xSiH manifold from consideration in the MPE excitation of visible photoluminescence from PS based upon the observed IR spectra in Fig. 2 is simply unrealistic. It is to be emphasized that the infrared spectra for these moieties will extend at least across the range 2150–2300 cm^{-1} easily encompassing the higher frequency band in Fig. 2(d).

As MPE through the vibrational manifolds of SiH_x and $OSiH_x$ induces luminescence, the result suggests that surface species are involved in the pumping process. In fact the results of Chin *et al.*[7] suggest that the luminescence observed by Wang *et al.*[6] using a 1.064 μm pump results from a direct three photon excitation which, at 0.353 μm, is virtually coincident with the peak in the PS photoluminescence excitation spectrum (PLE). This, in turn, suggests that the 1.3 μm PL spectrum also results from a three photon excitation, albeit at 0.433 μm. Finally, we suggest that the 0.532 nm excitation may indeed result from a two photon process at $\sim$266 nm. In fact, we have found that the fourth harmonic excitation from a Nd:YAG laser operating at this wavelength can readily produce the 600–800 nm PS photoluminescence spectrum.[8(c)]

ACKNOWLEDGMENTS

We gratefully 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 National Laboratory.

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