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Defect study of light-emitting HCl-treated porous silicon

S. M. Prokes and W. E. Carlos
Naval Research Laboratory, Washington, D.C.

Lenward Seals and James L. Gole
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430

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Electrochemically etched porous silicon (PSi) samples have been exposed to a $3M$ HCl solution for set time intervals, resulting in a stable and enhanced luminescence from this material. These samples were examined using photoluminescence (PL), electron spin resonance (ESR), and Raman spectroscopy. The Raman chemical disorder component is found to increase significantly with increased HCl exposure, tracking also with the increased PL intensity. In contrast, a significant drop in the nanocrystalline Raman component is monitored, suggesting that the number of silicon nanocrystallites decreases with increasing exposure to HCl. ESR spectra of these treated PSi samples indicate the presence of an NL8 type of oxygen shallow donor, which tracks extremely well with the increasing PL emission and the amount of chemical disorder induced with increasing HCl exposure.

INTRODUCTION

Visible-light emission in the orange-red and red region of the spectrum has been reported in a variety of silicon-based nanostructures, including porous silicon (PSi) nanostructures,[1,2] oxidized Si nanoclusters,[2–5] nanocrystalline Si/SiO_2 (nc-Si/SiO_2) films deposited by plasma chemical vapor deposition[6] (CVD), and Si nanowires.[7] The material most studied, however, has been PSi. The optical behavior in this material has been interpreted in terms of two very different types of mechanisms: quantum confinement[1] and models related to surface species[8–14] such as the emission from SiH_x or polysilanes,[8,9] siloxene,[10] or silanol groups,[12] Si band-tail states,[11] oxygen-related defect centers,[13] and silanone (Si=O) related entities,[14] the latter two of which may be closely correlated.

From the defect studies in porous silicon, there are several defect structures that have been reported, including the Si dangling bond center, prototype of which is the P_b center,[15] an E' center (oxygen vacancy),[16] the oxygen shallow donor (SD),[17] and an *EX* center (silicon vacancy).[16] Although it has been reported that the P_b center leads to an increase in nonradiative recombination, thereby decreasing the visible PL emission,[11] a direct link has been reported between the orange-red–red room-temperature PL intensity observed in freshly made and oxidized PSi and interfacial oxygen-related defect centers (SD and *EX*).[18]

It has been shown previously[19] that the exposure of freshly made PSi to an HCl solution varying in molarity from $0.2M$ to $6M$ can result in a much enhanced red-emission intensity as well as a long-term stability (after treatment with methanol) in the atmosphere. In this manuscript, we will present results of a $3M$ HCl treatment of PSi samples, with the perspective of tracking the changes in the nanocrystalline and amorphous fractions of the samples (Raman spectroscopy), the PL emission energy and intensity (PL), and the defect density (ESR) with increasing HCl exposure time. We will also show that despite the fact that the fraction of the nanocrystalline component comprising the PSi structure significantly decreases with increased HCl exposure, the PL emission intensity increases considerably and scales well with the increasing disorder fraction and the increasing oxygen shallow donor concentration. These results cast doubt on the quantum confinement model, while giving further support to the suggestion that an emitting chemical defect structure, comprised of a core Si=O entity,[13,14] gives rise to the observed PL.

EXPERIMENT

The PSi samples were prepared by standard electrochemical etching of 1-Ω cm *p*-type Si(100) wafers for 30 min at a current density of 14 mA/cm^2 in a 25% hydrofluoric acid (HF)/methanol solution. While a number of the samples were exposed to a $3M$ HCl solution through continuous soaking for periods of one or two weeks following the initial etch cycle, several additional samples remained untreated. The fresh samples referred to in the text are PSi samples that were freshly etched and analyzed within one hour. All samples were examined using Raman spectroscopy, photoluminescence (PL) excited using the 488-nm Ar^+-ion laser line, and cutoff filtered at 550 nm, and electron spin resonance (ESR), performed at 20 K, with and without tungsten lamp illumination. Further experimental details have been published elsewhere.[13,15]

RESULTS AND DISCUSSION

The Raman spectroscopy was performed on freshly made PSi and samples treated for one or two weeks in $3M$ HCl. Figures 1(a)–1(c) represent Raman spectra for these three types of samples. The Raman signal for all the PSi samples is blueshifted from that of bulk Si, and increases in width [full width at half maximum (FWHM)] with increasing HCl exposure.[19(b)] The fits for the individual Raman spectra are also depicted in Figs. 1(a)–1(c). The Raman spectrum for

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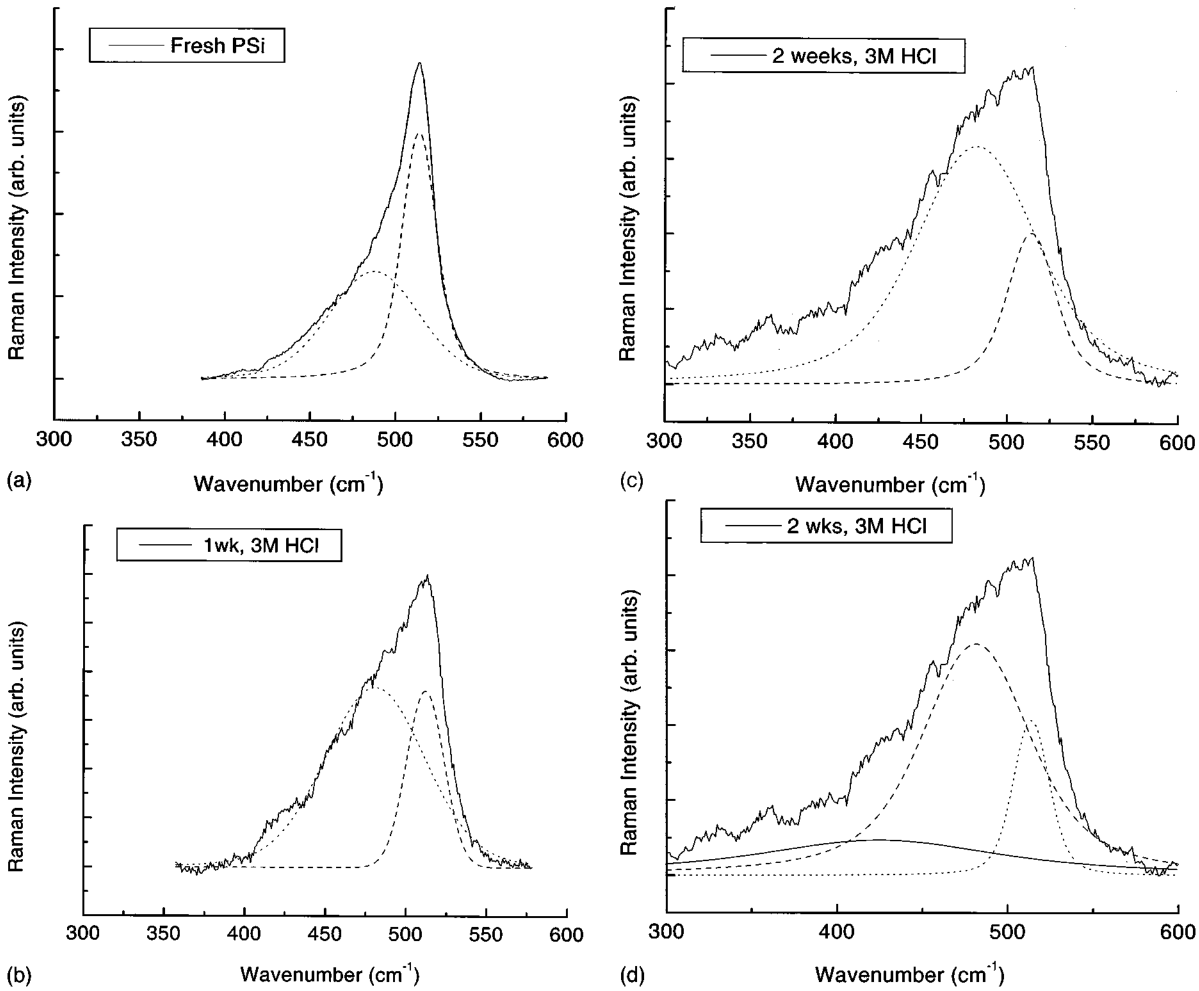


FIG. 1. Raman spectra and peak fits for (a) untreated PSi sample, (b) PSi after one-week treatment in 3M HCl, (c) PSi after two-week treatment in 3M HCl, and (d) PSi after two weeks in HCl showing a peak fitting line corresponding to SiO$_x$.

freshly formed PSi is comprised of two major peaks, a sharper one (at around 513 cm^{-1}) is associated with nanocrystalline silicon and a broader peak (at around 480 cm^{-1}) is associated with disordered silicon.[20] The Raman spectrum that results after a one-week HCl exposure produces a small shift of the nanocrystalline component to about 511 cm^{-1}, while a two-week HCl exposure results in a nanocrystalline component position close to 513 cm^{-1}. The amorphous silicon disordered component remains in the vicinity of 480 cm^{-1}. The standard error for the fits of the crystalline peaks for all the samples was always around 10%, while the error for the disorder peaks was always in the 15–18 % range for all samples fit.

What is striking in these figures is the significant growth in intensity of the disordered fraction with increased exposure to the HCl solution. In fact, the ratio of the integrated area for the disordered to nanocrystalline peaks is 0.77 for the fresh sample, 2.8 for the sample treated for one week in HCl, and 3.6 for the sample treated for two weeks in HCl. Coincidentally, the FWHM changes from 57 cm^{-1} for the freshly made PSi to 73 cm^{-1} for a one-week HCl exposure, to roughly 85 cm^{-1} for a two-week HCl exposure. Since Raman spectroscopy is a measure of local order, the width (FWHM) increase of this disordered feature suggests that chemical disorder is being introduced into the amorphous silicon component due to the HCl treatment. This could occur through the incorporation of O, H, or Cl species into the disordered Si network in what is, at the very least, a disorder-enhancing process.

Although the spectrum for the two-week treated samples is reasonably fitted by the sum of nanocrystalline and amorphous peaks, an improvement to the fit below 450 cm^{-1} can be achieved if a third broad feature, centered at about 430 cm^{-1}, is added [Fig. 1(c)]. This, in fact, is the region from which one would expect to observe contributions from the rocking band vibration in SiO$_2$, centered at 450 cm^{-1}.[21] However, it has been reported that large redshifts of the vibration frequency and the FWHM occur for material that is significantly off stoichiometry, corresponding to SiO$_x$, where x is significantly less than 2.[22] Thus, we suggest that the apparent additional 430-cm^{-1} feature present after a two-week exposure to HCl is the signature of SiO$_x$, whose presence increases with increased HCl exposure time. Further information on the incorporation of O, H, and Cl constituencies, as well as on the formation of SiO$_x$, is currently being obtained from Fourier-transform interferometry (FTIR).

We have used the 488-nm line of the Ar$^+$ laser to excite PL from the HCl-treated PSi samples. The spectra depicted in Fig. 2 were obtained using a 550-nm cutoff filter, which was necessary to suppress scattered laser light. The observed

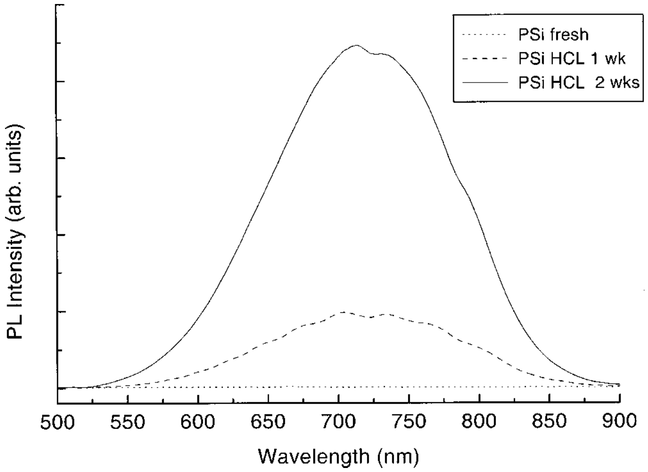


FIG. 2. Photoluminescence spectra for PSi samples treated for various time periods in 3*M* HCl. The data were taken using the 488-nm line of the Ar^+ laser and a 550-nm cutoff filter.

spectra are therefore localized to the orange-red–red emission region and do not reveal those contributions from the shorter-wavelength ‘‘green’’ emission feature[19(b)] that has previously been associated with a silane based silicon oxyhydride precursor state.[23]

After optical pumping with the 488-nm Ar^+ laser, the PL from a freshly made PSi sample is not easily measurable, nor is the PL from PSi samples that were not exposed to HCl but were aged in the atmosphere for two weeks. However, the PL for the one-week HCl-treated sample increases markedly, and the PL for the two-week-treated sample is almost 5 times that for a one-week exposure (Fig. 2). While we observe that no shift in the PL spectrum occurs for any of the HCl-treated samples, a clear shift in the nanocrystalline size is evidenced from the Raman crystalline peak position. Thus, it appears that no correlation between the PL intensity and the crystalline particle size is evident but a correlation between the PL intensity and the amount of (O, H, Cl)-containing chemically disordered amorphous silicon exists.

In obtaining the ESR data, the same samples whose Raman and Ar^+ pumped PL spectra are shown in Figs. 1 and 2 were evaluated in order to avoid possible sample to sample variations. The ESR study was performed with and without tungsten lamp illumination. A typical signal for the two-week-treated samples exposed to tungsten lamp illumination is shown in Fig. 3(a). Dark samples [Fig. 3(b)] show only a single broad signal at $g \approx 2.0055$, which has been identified as a silicon dangling bond[15] (P_b center) in this system. This feature is also visible in the illuminated scan albeit with a somewhat greater intensity. However, a second, much more intense feature appears under illumination, which has an average g value of 1.997. From previous studies, where this feature has been reported in freshly made as well as open-circuit etched PSi, we identify the ESR signal with that of an oxygen shallow donor (SD).[17]

We can suggest a possible explanation for the behavior of these defect centers in the absence and presence of light. The P_b center is amphoteric with a +/0 transition approximately 0.2 eV above the valence band and a 0/− transition about 0.3 eV below the conduction band.[24] The Fermi level of the sample is below the +/0 transition of the P_b center (well below the 0/+ transition of the SD's). At low temperatures, the SD is neutral and diamagnetic and the P_b center is positively charged and also diamagnetic. Optical excitation can remove an electron from the SD, making it positive and paramagnetic. The P_b center may then capture the electron, neutralizing it and also making it paramagnetic. Following this mode of preparation, the two centers in the absence of further illumination remain in these metastable states because there are no free carriers available to reverse or continue the process. Also, because of local inhomogeneous bandbending in the Si nanocrystals, even in the absence of illumination, some of the P_b centers will be neutral, as we have observed.

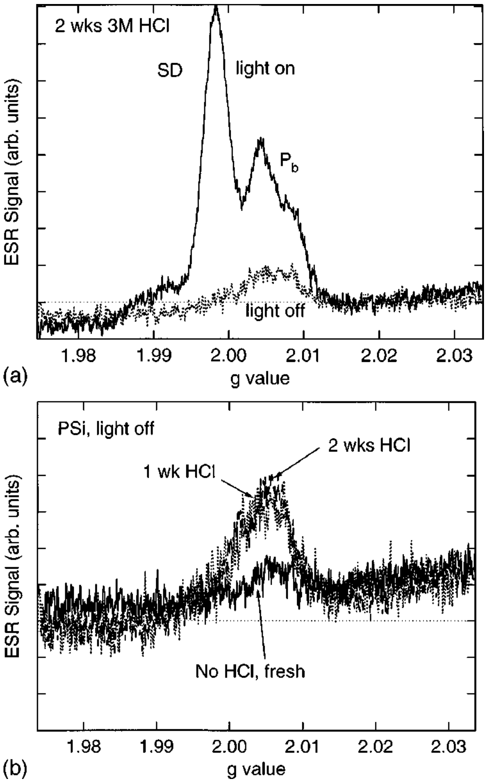


FIG. 3. Typical ESR spectra taken at 20 K for (a) two-week-treated PSi sample, with and without tungsten lamp illumination, and (b) all three types of sample taken with no illumination.

Figure 4 demonstrates the angular dependence of the SD for the two-week HCl-treated samples. This angular dependence exhibits an identical behavior to the SD's reported previously, which have been identified as an NL8 type[17] of thermal donor. Since the SD identified here is the same as that identified previously in regularly etched PSi samples, it seems unlikely that the outlined HCl treatment leads to the formation of a different SD, which bears Cl^- incorporation in its nearest-neighbor configuration. Here, both defects appear to be NL8 SD's, which consist of a silicon vacancy and oxygen nearest neighbors. Thus, the role of the HCl in this case may not be to contribute a chloride to the active center but rather to enhance the formation of suboxides/oxides leading to an enhanced formation of the SD's in the interfacial region.

While the ESR and Raman data presented in this study suggest (1) the presence of SD defect sites associated with silicon-oxygen bonds and (2) an increase in these defect sites commensurate with an increase in the disordered silicon

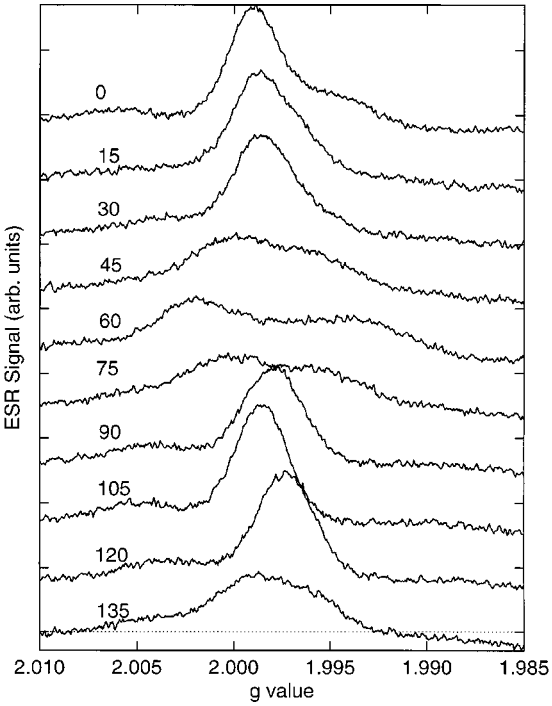
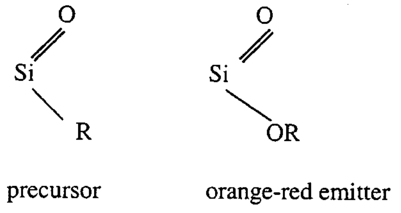


FIG. 4. Angular dependence (with respect to [100]) of the oxygen shallow donor (SD) defect in the two-week HCl-treated PSi sample.

structure, these probes do not indicate the nature of the ligands that might be attached to the silicon-oxygen core. We have previously considered[23] that fluorophors corresponding to silanone-based silicon oxyhydrides might account for the PL from porous silicon. We have suggested[23] that the ''green'' precursor state PL, which has been associated with porous silicon, be correlated with an —*R* group bound silanone and that the oxidative transformation of the —*R* group bound ligand to a corresponding —*OR* group can account for the formation of the long-lived (triplet state) orange-red emitter, viz.,



In fact, evidence has been obtained, in a recent near field scanning optical microscopy (NSOM) study[25] using 488-nm excitation, which suggests that this oxidative treatment can be enhanced through the excited-state oxidation of the long-lived precursor state. While clear evidence for this process is not apparent in the present study, its contribution to the formation of the orange-red emitter in both the 488-nm Ar$^+$ PL excitation (Fig. 2) and tungsten-lamp-illuminated ESR experiments (Fig. 5) must be kept in mind.

The behavior of the SD's as a function of HCl exposure time is indicated in Fig. 5. The figure suggests that very few, if any, SD's are present in the freshly formed material, while the SD ESR signal grows with increasing HCl treatment. It should be noted that a dark scan of *all those samples* considered produced only the P_b signal, depicted in Fig. 3(b) (also reported previously).[13]

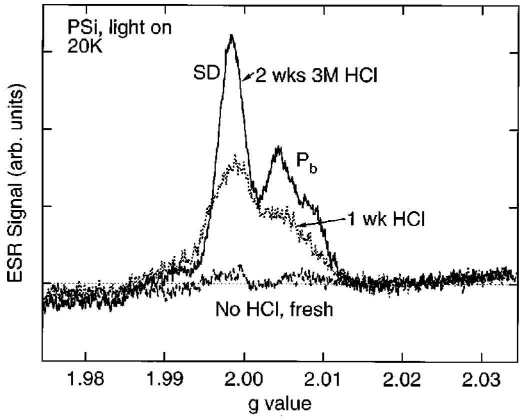


FIG. 5. Behavior of the SD's as a function of HCl exposure time. Experiments were performed at 20 K with tungsten lamp illumination.

Since the Raman, ESR, and PL probes have been applied to identical samples, let us examine the trends which appear for the three sets of data which we have considered. Figure 6 corresponds to a plot of the intensity changes of the Raman crystalline and disorder fractions (obtained from Fig. 1), the ESR signal intensity of the SD defects (from Fig. 5), and the red PL intensity as a function of exposure to the 3*M* HCl solution for up to two weeks (from Fig. 2). Similar results were obtained for different sets of PSi samples with and without HCl treatment. The PL intensity, ESR SD intensity, and the Raman disorder fraction all increase with increasing HCl exposure, while the Raman crystalline fraction actually decreases with HCl treatment and thus *decreases* with increasing PL intensity. Since this crystalline component is attributed to the nanocrystalline particles present in these silicon-based samples, the number of these particles is decreasing while the PL intensity is increasing. Furthermore, as we have noted, no PL shifts are observed, yet the particle sizes obtained from the Raman data do change, although no obvious trend is established. These results are clearly inconsistent with the quantum confinement model. It is interesting

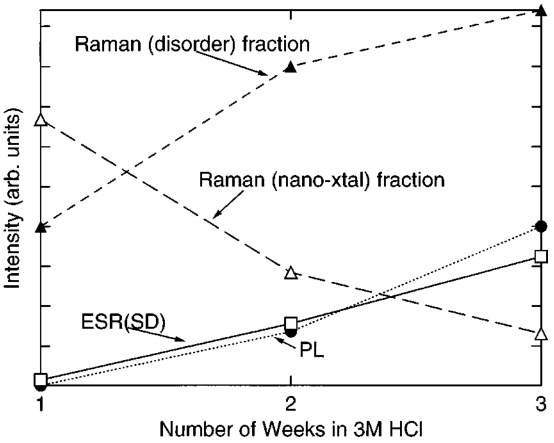


FIG. 6. Plot of the nanocrystalline and disordered Si fraction, SD intensity obtained from ESR, and PL intensity as a function of exposure time in the 3*M* HCl solution.

to note, however, how the SD intensity, the PL intensity, and the Raman disorder fraction track with increasing HCl exposure. In fact, the SD's have been previously identified as clusters of nonbridging oxygen-hole centers (NBOHC's), which are optically active in the red portion of the spectrum[26] and which have been associated with the red PL exhibited by both freshly made and oxidized porous silicon.[27] The fact that these color centers are also present in the intensely luminescing HCl-treated PSi, scale with the PL intensity, and scale with the degree of disorder (presumably increasing chemical disorder due to the presence of O, H, and Cl) gives further support to a model based in large part on oxygen-defect luminescence[13] (NBOHC) and its potential correlation with light-emitting silanone-based silicon oxyhydrides.

CONCLUSION

PSi samples have been electrochemically etched and exposed to a 3*M* HCl solution for given time intervals, resulting in a stable and an enhanced PL. These samples were evaluated using Ar^+-ion excited PL, electron spin resonance, and Raman spectroscopy, and the results of these studies showed several interesting trends. It has been demonstrated that the Raman chemical disorder fraction increases significantly with increased HCl exposure, commensurate with the PL intensity. In contrast, a significant drop in the crystalline Raman fraction is monitored, suggesting that the number of nanocrystallites decreases with increasing HCl exposure. The ESR results suggest the presence of an NL8 type of oxygen shallow donor, which tracks extremely well with an increasing PL emission and the amount of chemical disorder noted with increasing exposure time. These SD's have previously been identified in freshly made and open-circuit etched PSi samples and associated directly with clusters of interfacial NBOHC's, previously suggested as the source of the visible red PL in this system.[13,17] The fact that the PL intensity, chemical disorder (O, H, and Cl incorporation), and SD signal track closely while the PSi crystalline component signal tracks *inversely* to the resulting PL emission intensity lends support to a model consistent with a surface defect NBOHC that might well support a silanone-based silicon oxyhydride emitter.

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