

2009

Stain Etching with Fe(III), V(V), and Ce(IV) to Form Microporous Silicon

M E. Dudley

Kurt Kolasinski

West Chester University, kkolasinski@wcupa.edu

Follow this and additional works at: http://digitalcommons.wcupa.edu/chem_facpub



Part of the [Chemistry Commons](#)

Recommended Citation

Dudley, M. E., & Kolasinski, K. (2009). Stain Etching with Fe(III), V(V), and Ce(IV) to Form Microporous Silicon. *Electrochemical and Solid State Letters*, 12(4) <http://dx.doi.org/10.1149/1.3074333>

This Article is brought to you for free and open access by the College of Arts & Sciences at Digital Commons @ West Chester University. It has been accepted for inclusion in Chemistry by an authorized administrator of Digital Commons @ West Chester University. For more information, please contact wcressler@wcupa.edu.



Stain Etching with Fe(III), V(V), and Ce(IV) to Form Microporous Silicon

Margaret E. Dudley^{a,*} and Kurt W. Kolasinski^{***,z}

Department of Chemistry, West Chester University, West Chester, Pennsylvania 19383, USA

Stain etchants made from (HF + V₂O₅) or (HF + FeCl₃·6H₂O + HCl or H₂SO₄) exhibited virtually no initiation time before the formation of porous silicon. Etching with Fe(III) solutions for extended periods resulted in a unique dual layer structure that can reach a thickness >10 μm and exhibited not only red-orange but also green photoluminescence (PL). Etching with (CeF₄ + H₂SO₄) produced extremely uniform films. Visible PL was observed immediately after etching except for those films produced with (CeF₄ + H₂SO₄), which required several days of air exposure before bright and robust PL developed.
© 2009 The Electrochemical Society. [DOI: 10.1149/1.3074333] All rights reserved.

Manuscript submitted October 29, 2008; revised manuscript received December 31, 2008. Published January 29, 2009.

Electroless etching to create either nanocrystalline microporous silicon or silicon nanowires takes several forms.¹ Stain etching is a technique that involves an etchant composed of an oxidant in an acidic fluoride solution. When the concentrations are appropriately adjusted, porous film formation rather than electropolishing takes place. Stain etching has the potential advantage of being simple and inexpensive. It can also be performed on silicon substrates of arbitrary shape, for example, on mesoscopic pillars.^{2,3}

Stain etching has a bad reputation because the most commonly used oxidant is a nitrate (or nitrite). The use of nitrates leads to bubble formation, inhomogeneous films, and irreproducible results. Little control over the photoluminescence (PL) wavelength is observed. The films are generally not much over 1 μm. An annoyance is that the etchants often exhibit variable induction times that can be 15 min or more. Sodium nitrite has been added to avoid this induction time;⁴ however, it tends to enhance bubble production.

Recognizing that the role of the oxidant is to inject holes into the valence band, thereby initiating the reactions that engender porous silicon (por-Si) formation, and that the reactions do not directly lead to the formation of a gas, Nahidi and Kolasinski⁵ suggested that bubble generation could be avoided by using an oxidant that involves a transition metal ion. They introduced a particularly useful oxidant Fe³⁺ and showed that it could be used to produce uniform films in the absence of bubble formation. However, they still experienced problems with a variable initiation time.

During this study, we became aware of the work of Solomon et al.⁶ who applied stain etching with a FeCl₃ + HF + HCl solution to the formation of porous hydrogenated Si from hydrogenated microcrystalline Si deposited by plasma-enhanced chemical vapor deposition. Their starting material is much different than the single-crystal Si wafers used here; nonetheless, they were able to produce brightly photoluminescent films after very short etch times (<1 min).

Our two primary objectives in this report are to demonstrate that stain etching with Fe³⁺ as an oxidant is significantly more versatile than previously thought and to show that the V(V) and Ce(IV) oxidation states can also be used as extremely effective oxidants. V(V) exhibits essentially instantaneous por-Si formation and Ce(IV) produces the most uniform films yet observed. These films exhibit PL and the orange-red PL is long-lived. The initiation time of Fe³⁺-based etchants can be reduced to 1 min or less by the addition of concentrated HCl or H₂SO₄. Unstable green emission has also been observed from films etched for extended periods (>4 h).

* Electrochemical Society Student Member.

** Electrochemical Society Active Member.

^a Present address: Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093, USA.

^z E-mail: kcolasinski@wcupa.edu

Experimental

All samples were etched from Si(100), Czochralski grown, B-doped, p-type prime grade wafers with 14–22 Ω cm resistivity and 500–550 μm thickness. All solutions were aqueous. All etching was performed at room temperature for the Fe(III) and V(V) solutions. The oxidants were introduced either by the addition of FeCl₃·6H₂O to provide Fe(III) or V₂O₅ to produce V(V). Fluoride was supplied from 48% HF(aq). Ce⁴⁺ precipitated to form CeF₄ when added to aqueous HF. However, we have found that Ce⁴⁺ was forced into solution by dissolution of CeF₄ in concentrated H₂SO₄. When indicated, concentrated HClO₄, HCl, and H₂SO₄ were used. We only tested the effects of concentrated acid on the Fe(III)-based etchants. Therefore, to simplify our notation, we refer to FeCl₃·6H₂O + 48% HF as the Fe(III) etchant; FeCl₃·6H₂O + 48% HF + concentrated HClO₄ as Fe(III) + HClO₄ or simply HClO₄ etchants, etc. The etchants containing V₂O₅ are referred to as the V-based etchants. The etchants formed from CeF₄ + H₂SO₄ are referred to as the Ce-based etchants. After etching, the samples were rinsed several times, first in water and then in methanol or ethanol. Critical point drying (CPD) was performed in a Tousimis AutoSam-Dri 815 critical point drier in which the initial solvent (ethanol) was replaced by a supercritical fluid of ethanol and CO₂.

Scanning electron microscopy (SEM) was performed with an FEI Quanta 400 ESEM, at a voltage of 2–15 kV with a working distance of 10–15 mm. Imaging was usually performed in a background of ~100 Pa of water in an environmental SEM mode. The SEM operated with integrated Oxford INCA energy dispersive X-ray spectroscopy (EDS). PL and PL excitation spectroscopies were performed on a Cary Eclipse fluorescence spectrometer, with slit widths set for 5 nm resolution and filtering on both the emission and excitation. 350 nm light, which has a penetration depth <100 nm, was used to excite PL in the spectra shown below. PL peak positions were determined by fitting the top of the peak to a Gaussian profile and are reported as the center of the resulting Gaussian fit. While PL spectra were observed to change over the course of several hours of air exposure or several minutes of UV exposure, they did not change over the course of the time scale of a minute or so required to acquire a single spectrum.

Results and Discussion

Addition of concentrated acids to Fe(III)-based etchants.— Starting with the Fe(III) etchants of Nahidi and Kolasinski,⁵ we began a combinatorial approach for optimization of the solution composition. We used either 1.37 or 1.65 g of FeCl₃·6H₂O added to a solution of 48 wt% HF + concentrated acid (HClO₄, HCl, or H₂SO₄). The sum of the volume of the HF + acid always equaled 10.0 mL; hence, the Fe(III) concentration was either 0.507 or 0.610 mol dm⁻³, respectively.

Addition of HClO₄, HCl, and H₂SO₄ produced more stable and reproducible results than stain etchants composed of just Fe(III) + HF. The addition of acid changed the induction time. In all three

cases, the induction time was reduced to <5 min and became less variable when compared to Fe(III) + HF etchants. The induction time varied with the concentration of Fe(III) and acid. Of the three, H_2SO_4 had the shortest induction period, usually <1 min. Frequently, the initiation of por-Si formation in H_2SO_4 etchants was remarkably uniform across the entire surface as demonstrated by a uniform color change across the whole wafer. More commonly and especially in the other etchants, a color change began in one part of the crystal and then swept across the remainder. All three etchants produced thick ($>1 \mu\text{m}$) layers of brilliantly photoluminescent por-Si. One major disadvantage of the HClO_4 etchant, but not the HCl and H_2SO_4 etchants, was that a precipitate formed when etching was performed for long periods, particularly if Ar is not used.

Extended etch duration in Fe(III)-based etchant.— Previously, Nahidi and Kolasinski⁵ only examined the results of etching for ≤ 30 min; here, we investigated longer etch durations. It was important to exclude air from the reaction vessel to obtain reproducible results; therefore, we displaced the air with Ar and the beaker was covered during etching.

Etching for >3 h in HClO_4 , HCl , and H_2SO_4 [or even longer times for Fe(III) + HF without added acid] led to a remarkable change in the film structure as shown in Fig. 1. The film shown in Fig. 1 was produced by etching for 22.5 h in an etchant composed of 1.37 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + 3 mL H_2SO_4 + 7 mL HF and was subjected to drying in flowing Ar after a final rinsing step in methanol.

Before drying, the film had a bronzy appearance. The color was mostly uniform, and the crystal had a shiny appearance, indicating a uniform flat film. During drying, the film took on a rough golden brown appearance. As Fig. 1 demonstrates, the roughening resulted from cracking and exfoliation. Closer examination of Fig. 1 revealed that only the upper half of the film exfoliated, the initial thickness of which was over $12 \mu\text{m}$. A film that exceeded $6 \mu\text{m}$ in thickness remained attached to the substrate. These films are far thicker than the $\leq 1 \mu\text{m}$ thickness usually associated with stain-etched films. The exfoliated flakes appeared much brighter in the micrographs because they were more susceptible to charging.

The film morphology was further investigated as shown in Fig. 2. We etched a Si substrate in 1.37 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + 3 mL HClO_4 + 7 mL HF for 27 h. The film was then rinsed and dried using CPD. The film retained its bronzy, shiny appearance after CPD. The film was then cross sectioned by cleaving. The upper and lower interfaces of the $\sim 4 \mu\text{m}$ thick film are sharp and flat (Fig. 2a). Note that the upper portion of the film appeared brighter, indicating a higher degree of charging. This could result from the upper portion of the film having a lower conductivity because it had a higher porosity.⁸

A drop of water was then placed on the cross-sectioned edge of the sample and the sample was dried in air. Drying caused significant capillary forces to build up, and similar to the results of Bellet and Canham,⁹ Cullis and Canham,¹⁰ and Kolasinski et al.,¹¹ these forces significantly altered the film morphology. Figures 2b and c show that capillary forces cracked and partially exfoliated the top layer of the film. Figure 2c follows the crack back to its origin to show that the crack was rough rather than a smooth cleave. The brighter upper part detached from the bottom of the film. We conclude that the upper part was mechanically less stable than the bottom of the film because it had a higher porosity.

Scanning electron micrographs revealed virtually no fine structure of the pores either in plan view or in cross section. Occasionally in plan view we observed a pore that was >50 nm diam, which was clearly a defect rather than an indication of the film's structure. For the most part, the film was composed of a homogeneous distribution of pores, which were smaller than the ~ 10 nm resolution of our SEM. We have performed preliminary transmission electron microscopy studies. These indicated that many pores may be on the order of 3 nm across. Using the formula of Bellet and Canham⁹ for the critical thickness of cracking, we estimate that the porosity of the upper layer must exceed $\sim 80\%$.

The dual layers had distinct optical properties. The upper layer

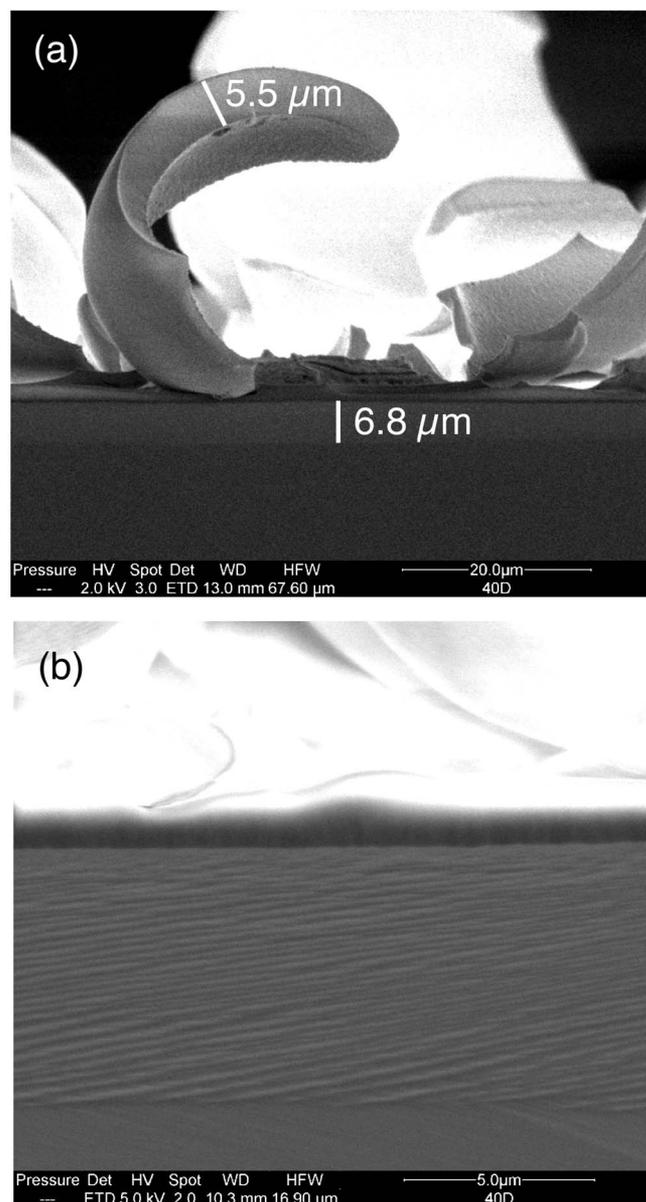


Figure 1. Two cross-sectional SEM images from porous silicon. Etching in 1.37 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + 3 mL H_2SO_4 + 7 mL HF for 22.5 h, under Ar; rinsing in water and methanol; and drying in a stream of Ar led to exfoliation and destruction of the upper part of the film. (a) The exfoliated region exceeded $5 \mu\text{m}$ in thickness, whereas (b) the film that remained intact and attached to the substrate exceeded $6 \mu\text{m}$ in thickness.

was less mechanically stable and completely removed by wiping with a Kimwipe or by a short (5–10 s) burst of ultrasonic radiation while the substrate was immersed in isopropanol. Removal of the upper layer was confirmed by eye from the change in the color and reflectivity of the substrate. Furthermore, removal of the upper layer created a photoluminescent powder. The upper and lower layers were optically distinct in that the PL was significantly bluer from the upper layer as compared to the lower layer. For a sample etched in 1.65 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + 3 mL HClO_4 + 7 mL HF for 5 h and dried in Ar, the peak shifted from 586 to 638 nm when the upper layer was removed. Assuming that the PL results from quantum confinement in silicon nanocrystals contained in the pore walls, bluer PL from

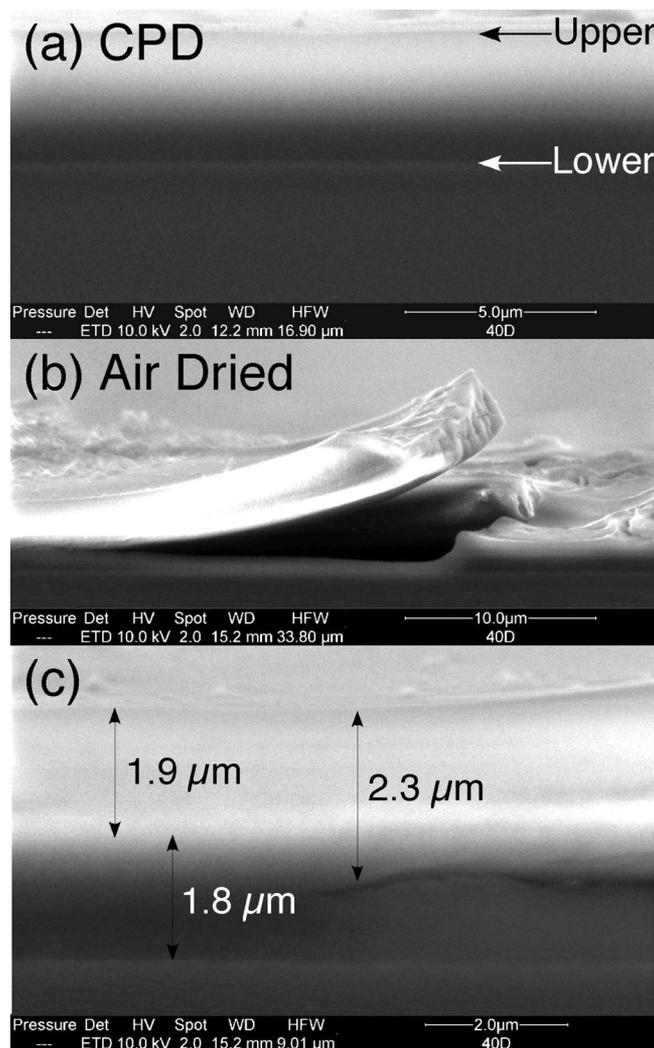


Figure 2. Cross-sectional SEM images of a por-Si film etched in 1.37 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + 3 mL HClO_4 + 7 mL HF for 27 h under Ar. (a) The film remained intact after CPD, and the upper and lower interfaces were both sharp. (b) A drop of water was placed on the film and allowed to dry in air. The top layer cracked and exfoliated. (c) Following the crack of the exfoliated region shown in (b) back to its origin, we see that the total film thickness was $\sim 4 \mu\text{m}$ and that the upper part of the film separated from the bottom part along an irregular crack.

the upper layer is also consistent with the upper layer possessing a higher porosity as this correlates with narrower walls and smaller crystallites.

For the HClO_4 , HCl, and H_2SO_4 etchants, the PL spectrum developed and changed for etch times up to ~ 8 h. The PL peak from the upper layer blueshifted as the etching time increased. It eventually reached the green region with a peak wavelength in the range of 520–530 nm (Fig. 3). This green emission was observed both when the film was immersed in water (never having been dried) and in air after drying. Whereas the green emission was stable at least for several days if samples were kept in a weakly acidic aqueous solution, the green emission faded when samples were exposed to air.

Simple quenching of the green PL by gaseous O_2 is not consistent with the following observations: (i) For a sample dried in Ar, the green PL was not immediately quenched by exposure to air. Instead, the green PL faded slowly over the course of 15–30 min. (ii) For a CPD sample, the PL was more stable and only faded over a period of hours. If quenching by O_2 were responsible for the disappearance of the green PL, the behavior should not depend on

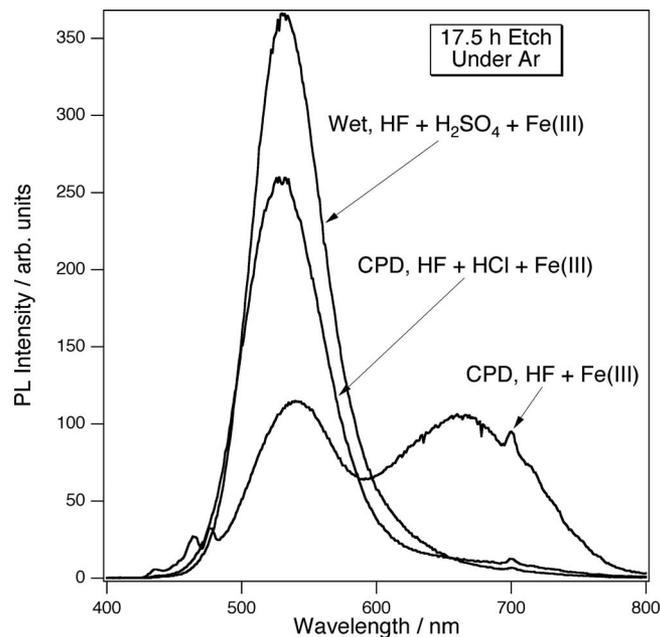
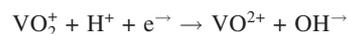


Figure 3. Etching >8 h leads to a significant blueshift in the PL. In the absence of added HCl or H_2SO_4 , the development of the peak near 530 nm was significantly slower. The samples were etched for 17.5 h with 1.65 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ added to 10 mL HF or 1 mL HCl + 9 mL HF or 1 mL H_2SO_4 + 9 mL HF.

the drying conditions and the quenching should be immediate upon exposure to air. Instead, the quenching of the green PL was more likely the result of a slow oxidation process induced by the dissociative adsorption of O_2 on the H-terminated surface of por-Si. We surmise that the superior structural integrity, and associated lower structural defect density, of CPD por-Si compared to Ar-dried por-Si reduced the dissociative sticking coefficient of O_2 , the oxidation rate was therefore lower, and the CPD films exhibited green PL for a longer period of time.

The Fe(III) + HF etchant also produced green-emitting films; however, it took significantly longer to do so. Even at 17.5 h of etching, such a film exhibited both the green PL peak and a red peak (Fig. 3). Unlike the green peak, the red peak faded only a little or not at all with air exposure. Some samples retained strong PL over a period of months, whereas others lost intensity over a period of days or weeks. X-ray dispersive spectroscopy performed in the SEM indicated that the air-exposed films contain only Si, O, and a small amount (if any) of F. Never was any Fe (or V or Ce for the films mentioned in the following sections), Cl or S found. Furthermore, IR absorption spectra of films freshly prepared in these etchants exhibited strong absorption peaks associated with Si–H bonds but gave no evidence for incorporation of O into the film immediately after rinsing and drying. The observations are consistent with results of anodic etching to produce por-Si in which the surface remains predominantly H-terminated throughout with some F atoms penetrating into the Si lattice or else being present in the form of physisorbed etched products.¹² There is no evidence for the formation of compounds containing anything other than Si and H.

V(V)-based etchant.— We mixed 0.28 g of V_2O_5 with 10 mL HF ($0.154 \text{ mol dm}^{-3}$ in V_2O_5). V_2O_5 dissolves yielding the V(V) oxidation state in the form of VO_2^+ . At 1.0 V, E_0 is sufficiently positive to inject holes into the Si valence band according to the half reaction⁷



This etchant led to almost immediate (<5 s) initiation of uniform por-Si formation in the absence of bubble generation. In Fig.

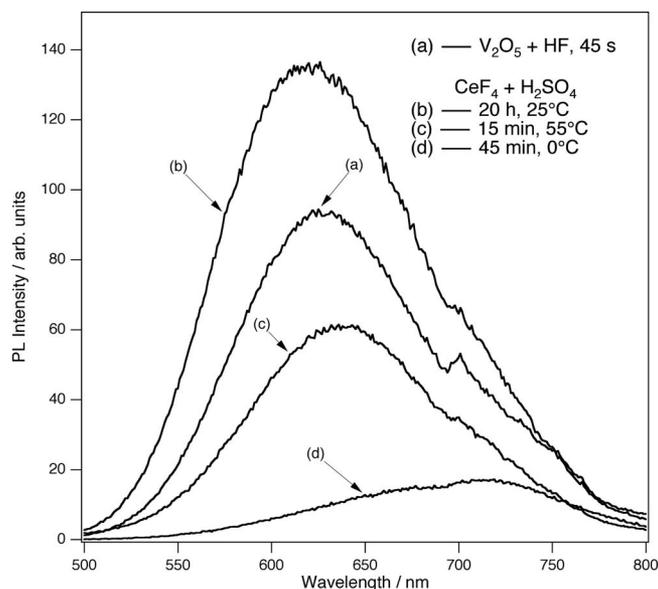
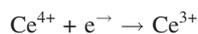


Figure 4. The PL spectra of (a) a film etched for 45 s in a V-based etchant containing 0.25 g V_2O_5 in 10 mL HF; (b–d) samples produced in the Ce-based etchant made from a saturated solution of CeF_4 dissolved in (5 mL H_2SO_4 + 5 mL H_2O), (b) etched 20 h at 25°C, (c) etched 15 min at 55°C, and (d) etched 45 min at 0°C.

4a, the PL spectrum of a film etched for 30 s in the V-based etchant is shown. The PL from films produced in V-based etchants was consistently red to orange (peaking at 610–650 nm), intense, and long-lived (months without degradation). The peak in Fig. 4a is at 630 nm, but we have not yet ascertained if it is possible to systematically shift the PL peak wavelength based on etching conditions. No other etchant forms layers as rapidly. As confirmed by EDS and IR spectroscopy, the pristine films contain nothing but hydrogen-terminated Si.

Ce(IV)-based etchant.— CeF_4 is insoluble in water. However, we found that addition of CeF_4 to a solution of 5 mL water + 5 mL of concentrated H_2SO_4 leads to a solution with a color characteristic of the solvated Ce^{4+} ion. Obviously, the formation of various fluoride species (HF , HF_2^- , etc.) drives the dissolution of CeF_4 in strong acid. Dissolution is an activated process; therefore, the solutions must be heated to get the Ce^{4+} into solution. The Ce^{4+} ion has an E_0 value of 1.44 V, which is sufficiently positive to inject holes into the Si valence band according to the half reaction⁷



We investigated the etching of a solution composed of 0.5 g CeF_4 + 5 mL H_2SO_4 + 5 mL H_2O at temperatures of 0°C and $25 \leq T \leq 75^\circ C$ in 10° steps. Only a fraction of the CeF_4 dissolves. The formation of a uniform por-Si film without bubble formation was observed at all temperatures. Formation was slower at 0°C but occurred readily at all temperatures up to 75°C.

The color changes that occurred as etching proceeded were exceedingly uniform and gradual as observed by eye over the first 30 min of etching. The films produced were the most uniform we have observed with deep rich colors produced by white-light interference. Samples etched for ≤ 30 min did not exhibit visible or IR PL immediately after rinsing and drying. After four to five days of exposure to air, faint spots of PL develop. After more than seven days, strong, robust, visible PL grew in intensity. When the PL appeared, it was in the visible. PL did not start in the IR and blueshift into the visible. The strong PL was subsequently stable over a period of months. Samples stored under dry Ar did not develop PL after seven days. However, once removed from the dry Ar atmosphere,

these samples developed PL after several days of air exposure just like the samples exposed immediately to air. Although we do not have a fundamental explanation for the development of PL, most likely it is related air-induced oxidation in some way; however, other explanations may be possible. It is important to note that as confirmed by EDS and IR spectroscopy, the pristine films contained nothing but hydrogen-terminated Si.

Most samples were red or red-orange, peaking at ~ 640 nm, although some exhibit yellow-green PL, peaking as low as 605 nm (Fig. 4b–d). We continue experiments to determine whether there is a systematic reason for the spectral differences exhibited in Fig. 4b–d. The yellow-green PL was only observed with the harshest etch conditions (a 65 h etch and an etch at 75°C). The reddest PL (peaking at 710 nm) was observed from a sample etched at 0°C. If a sample was etched overnight in the solution, it exhibited visible PL immediately after rinsing and drying.

Conclusions

Fe(III)-, V(V)-, and Ce(IV)-based stain etchants can produce uniform photoluminescent porous silicon films in the absence of bubble formation. It is shown here that V_2O_5 and CeF_4 can be used to produce stain etchants. Both IR and EDS spectra unequivocally indicated that the films as formed contained only Si and H. The kinetics of film formation were completely different for the three solutions, which made direct comparisons based on etching time difficult. The V-based solutions produced por-Si with virtually no induction time before por-Si formation began on single-crystal substrates and it continued at a high rate. The induction time of the Fe(III) solutions was significantly reduced by the addition of concentrated acids, especially HCl and H_2SO_4 , which had induction times of ≤ 1 min, and steady etching afterward. When etched for ≥ 3 h, these films were several micrometers thick and the upper half or more had a significantly higher porosity than the lower layer. While all of these etchants produced films that were more uniform than those created by the standard nitrate-based stain etchants, the slow but steady etching in the Ce-based etchant created the most uniform films.

The PL spectrum of all these films exhibited the usual red/orange PL in the range of 630–700 nm for etch times < 3 h. However, as the dual layer structure formed in the Fe-based etchant, the PL from the upper layer continually blueshifted with increasing etch duration. Eventually, peak wavelengths as short as 520–530 nm were observed. The PL peak from the lower layer behaved much like what was observed at shorter etch times.

Thus, we speculate that there are two reactions occurring in the stain etchant. The first is the conventional stain-etching reaction, which forms por-Si as described by Nahidi and Kolasinski.⁵ The second reaction is a much slower chemical reaction that gradually increases the porosity and blueshifts the PL spectrum. The second reaction is similar to the reaction suggested by Canham¹³ in his original report of visible PL from high-porosity por-Si. Canham used a 6 h quiescent reaction in 40% aqueous HF to obtain visible PL in anodically etched por-Si. If the mechanism of dual layer structure formation is that of two competing reactions with different rates and with the ability to produce correspondingly different minimum size silicon nanostructures, then our films likely possess a porosity gradient from low at the bottom to high at the top. It is unclear whether this gradient is abrupt, as suggested by Fig. 1 and 2, or whether it is gradual. Nonetheless, the mechanical instability of the upper layer lends itself to facile production of copious quantities of photoluminescent, nanocrystalline porous silicon powder.

Acknowledgments

This work was supported by West Chester University, the Center for Microscopy Research and Training at WCU and the expert technical assistance of Frederick Monson. Felix Goodson and Michael Moran provided excellent advice with regard to various aspects of organic and inorganic chemistry, respectively. Brian Kelly and Justin Hartline contributed supporting experimental data. K.W.K. is grate-

ful for the support of Eckart Hasselbrink under Sonderforschungsbereich 616 "Energiedissipation an Oberflächen" for a research fellowship and stimulating discussions.

West Chester University assisted in meeting the publication costs of this article.

References

1. K. W. Kolasinski, *Curr. Opin. Solid State Mater. Sci.*, **9**, 73 (2005).
2. D. Mills, M. Nahidi, and K. W. Kolasinski, *Phys. Status Solidi A*, **202**, 1422 (2005).
3. D. Mills and K. W. Kolasinski, *J. Vac. Sci. Technol. A*, **22**, 1647 (2004).
4. E. Vázsonyi, E. Szilágyi, P. Petrik, Z. E. Horváth, T. Lohner, M. Fried, and G. Jalsovszky, *Thin Solid Films*, **388**, 295 (2001).
5. M. Nahidi and K. W. Kolasinski, *J. Electrochem. Soc.*, **153**, C19 (2006).
6. I. Solomon, K. Rerbal, J.-N. Chazalviel, F. Ozanam, and R. Cortès, *J. Appl. Phys.*, **103**, 083108 (2008).
7. R. C. Weast, Editor, *CRC Handbook of Chemistry and Physics*, Vol. 60, CRC Press, Boca Raton (1980).
8. B. Hamilton, J. Jacobs, D. A. Hill, R. F. Pettifer, D. Teehan, and L. T. Canham, *Nature (London)*, **393**, 443 (1998).
9. D. Bellet and L. Canham, *Adv. Mater. (Weinheim, Ger.)*, **10**, 487 (1998).
10. A. G. Cullis and L. T. Canham, *Nature (London)*, **353**, 335 (1991).
11. K. W. Kolasinski, M. Aindow, J. C. Barnard, S. Ganguly, L. Koker, A. Wellner, R. E. Palmer, C. Field, P. Hamley, and M. Poliakoff, *J. Appl. Phys.*, **88**, 2472 (2000).
12. K. W. Kolasinski, *Phys. Chem. Chem. Phys.*, **5**, 1270 (2003).
13. L. T. Canham, *Appl. Phys. Lett.*, **57**, 1046 (1990).