The Dependence of Silicon Reactivity on the Constituents of the Etchant Electrolyte and the Effect of Some Postetch Treatments on the Photoluminescence Properties of Porous Silicon.

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The cyclic voltammetry (C.V.) technique was used to study the electrode process of silicon in different etchant electrolytes. Also, similar anodizing solutions to the electrolytes used in the C.V. were used for fabricating porous silicon (PS) samples in the electrochemical cell and the effect of some postetch treatments on the photoluminescence (PL) properties of these PS samples were tested. The j-v relation showed that, up to ≈ 50% water in the etchant electrolyte, the critical current peak height in $HF:HCl:C_2H_5OH: H_2O$ *electrolyte is higher than the critical current peak height in* $HF:(CH_3)_2CO:H_2O$ *electrolyte, which is higher than the peak in* $HF:C_2H_5OH:H_2O$ *electrolyte. Also, the j-v relation in case of concentrated electrolytes (≈0.4 % water) was not the standard one for PS formation. These results were reflected in the PL properties of the fabricated PS samples. Water in the presence of HF had a magnified influence in the PL intensity of PS samples fabricated via anodization in concentrated electrolyte. A mechanism for Si dissolution in HF-acetone was proposed. The results were explained in terms of the model which attributes the PL to surface confined molecular emitters.*

1. Introduction:

Silicon received much more attraction since the discovery of efficient photoluminescence (PL) from electrochemically anodized silicon [1]. A large amount of worldwide work has been performed towards understanding the origin of the porous silicon PL (PS PL) [1-5]. Nevertheless, numerous fundamental questions remain concerning the physics of the formation of PS layers as well as the origin of luminescence.

Bulk crystalline silicon can be rendered porous by partial electrochemical dissolution of the silicon wafers surface in hydrofluoric acid based media. Many authors already discussed the role of water during preparation and after it [6-8]. The PL properties of PS depend on its chemical composition which could be changed either during preparation or after preparation (postetch treatment).

The goal of this work is to study the electrode process of silicon in different electrolytes aiming to elucidate the dependence of silicon reactivity on the type of the etching electrolyte. The roles of different postetch treatments on the PL properties of samples were also touched. The silicon reactivity study was carried out using the cyclic voltammetry (C.V.) technique in 1% HF based electrolytes. (No clear current peak could be observed on j-v curves in higher than 10% concentrated HF solutions due to the formation and evaluation of hydrogen bubbles at high current density [9]).

2. Experimental:

P^+-Si wafers with (111) surface orientation, with a resistivity of ≈0.015 Ωcm and thickness of about 450 µm, were used in this work. After each voltammogram, the PS layer was removed by immersion in 10 weight percent (w/o) aqueous solution of KOH for 10 s followed by rinsing in distilled water for 5 min. The wafer area exposed to the electrolyte was 0.237 cm^2 circular.

For PS preparation, we used the anodization under galvanostatic condition (electrochemical etching in an HF-based electrolyte) method[10]. The samples were anodized at current density of 19 mA/cm^2 for 20 min. Two sets of etchant electrolytes were used. The first set (the diluted one) consisted of $HF:C_2H_5OH:H_2O=2:1:1$, $HF:(CH_3)_2CO:H_2O=2:1:1$, and $HF:HCl:C_2H_5OH:H_2O=3:1:1:1$. The other set (the concentrated one) consisted of $HF:C_2H_5OH=1:1$, $HF:(CH_3)_2CO=1:1$, and $HF:HCl:C_2H_5OH=1:1:1$. Each set was used for fabricating three different samples. A 15ml capacity Teflon cell was used during the experiments. The Si wafer acts as the anode and the cathode is made of platinum. The sample was sealed through rubber O-ring, so that only the front side of it was exposed to the electrolyte.

The cyclic voltammetry measurements were carried out using a conventional three-electrode assembly (WE, CE and saturated calomel reference electrode SCE). A (Wenking LB 75L, Germany) potentiostat, Wenking MVS87, Germany voltage scanner and X-Y recorder were used. The reference electrode was connected to the electrolyte by means of a bridge made of polyethylene capillary tube filled with a saturated solution of KCl in agarose gel. The potential sweep was taken sufficiently slow (10 mV/sec). In the C.V. measurements; ethanol/HF/H_2O, acetone/HF/H_2O, and HCl/ethanol/HF/H_2O electrolytes were used. Both of PS fabrication process and C.V. measurements were done under illumination with visible light whose intensity was found to be

1670 Lux. During these measurements, HF (40%) was used. The surfaces of the porous silicon samples were observed using scanning electron microscopy (SEM), Jeol 1.00-S Japan.

As a check for PL upon completion of etching, the samples were viewed under ultraviolet (UV) lamp In the PL measurements, an Ar-ion laser (λ=488 nm) was used as an excitation source. The irradiation power was ≈ 20 mW.

3. Results

3.1. Cyclic Voltammetry

Fig.(1) collects typical current potential curves of p-Si in a mixture of HF, water and ethanol etchant solutions in the proportions: 1%HF: X% H_2O: (99-X)% C_2H_5OH, by volume. At $X \leq 3.3$, (Figs.1a &1b) a linear j-v relation is observed without difference between the forward and reverse scan. Increasing water content to X=6.6 (Fig.1c), a separation between the positive and negative scan starts to appear. Two poorly defined rudimentary peaks (J_1 & J_2) are hardly observed in the positive scan direction around 1.5 V and 3.0 V respectively, indicating the onset of pore formation reaction. Also, another small peak (J_3) starts to appear around 0.7 V in the negative scan direction. With a further increase of the water content, (X= 13.3 & 20), two peaks (J_3 & J_4) around 0.7 V and 2.6 V, respectively are revealed with negative potential scan (Fig.1d for X= 13.3). Furthermore, at $99 \geq X \geq 46.7$ in the positive scan direction, the anodic current increases with the electrode potential up to the first peak J_1 at

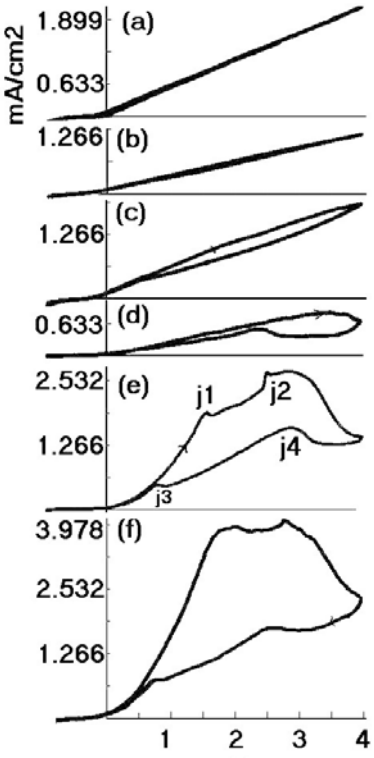


Fig.(1): Voltammograms obtained for p^+-Si electrode in {1%HF: X% Water: (99- X) %Ethanol} electrolytes.
a: X=0, b: X=3.3, c: X= 6.6,
d: X=13.3 e: X=73.3, f: X=99

around 1.5 V. As the potential is increased, the current decreases followed by a second broad, poorly defined peak (J_2). In the negative scan direction, the overall shapes of all these voltammograms ($99 \geq X \geq 13.3$) are rather similar. When the electrode potential is swept towards negative values, one observes first a constant current (plateau) value followed by a peak (J_4) around 2.5 V and a steep current fall. Then another narrow peak (J_3) is found around 0.5 V, followed by a current decrease again till zero potential. These j-v curves ($99 \geq X \geq 13.3$) seem to be a characteristic feature of the Si in diluted HF solution studied in the absence of flow [11]. This observed hysteresis in the C.V.curves could be a consequence of using an immobile electrode in the absence of flow. The increase of the water content from 20% to 53% has found to increase the peak current (J_1) in the voltammogram by a factor of two (Fig.3). The pure water/HF solution (X=99) gives the maximum peak height. A most striking feature is the linear increase of the Si oxidation current with the applied potential, most probably due to solution and semiconductor large uncompensated series resistance in the [1%HF: X%water: (99-X)%ethanol] electrolyte when $X \leq 3.3$. The mechanism of ionic transport in the anodic oxidation of silicon is rather disputed [12].

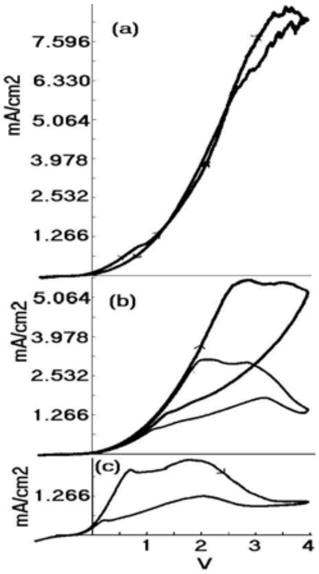


Fig.(2) Voltammograms obtained for p$^+$-Si electrode in {1%HF: (99-X) %(6HCl:8.8Ethanol): X% Water} electrolytes.
a: X=0, b: X=11.8, c: X= 83

The C.V. for Si in 1%HF: X%H_2O: (99-X) % $(CH_3)_2CO$ results in a very similar behavior to that of Fig.1 i.e. a linear increase of the silicon oxidation current with the applied potential at X=0 and the appearance of two broad current peaks around 1.6V and 2.5V in the positive potential scan in addition to two peaks in the negative scan around 0.7 V and 2.3 V at X>6.7.

Fig. (2) shows the C.V. for Si in 1%HF: (99-X)% (6HCl:8.8C_2H_5OH): X% H_2O etchant electrolyte. When X=0 (Fig.2a), a sharp rise of the anodic current followed by a small shoulder at about 0.8 V is observed. Then, the current increases very rapidly till about 3.4 V where little current variations are seen superimposed on a short plateau. On the reverse scan direction; the current diminishes sharply with some variations till around 2.5 V, followed by rise decay to the zero value. The observed hysteresis is limited. Adding water to the electrolyte X=11.8, (Fig.2b) causes the appearance of an-exponential current growth followed by a broad peak at around 2.5 V and a narrow plateau. Then a second broad peak is found at around 3.4 V followed by a second short plateau. In the negative scan direction, the current decreases with potential and only one current peak is observed at around 1.3 V. A second successive C.V. shows a typical one for Si in diluted HF solution, in the absence of flow, with lower current density values. This second sweep cycle indicates that the electrode surface condition is different from the first sweep cycle. With a further increase of the water content of the etchant solution (X>11.8), the C.V. curves have virtually similar shapes. The clear feature of these cyclic voltammograms, is the independence of the magnitude of the current peak on the water contents of the echant electrolyte when X>11.8.

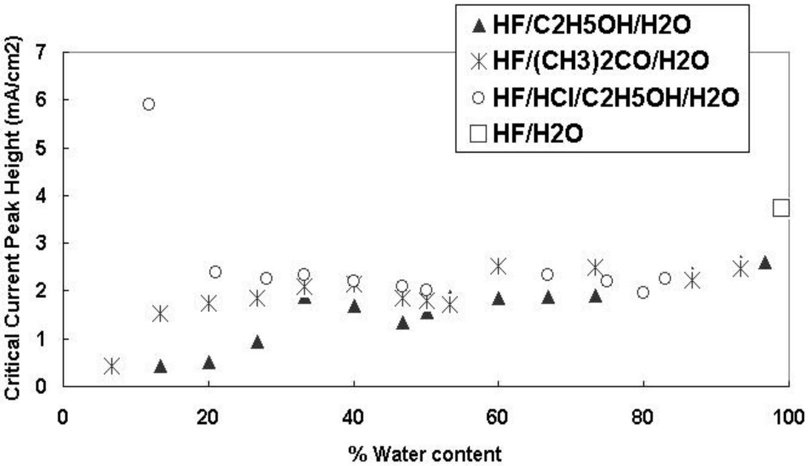


Fig.(3): Variation of the critical current peak height (J_1) as a function of the electrolyte water content for different etchant electrolytes.

In the above studied cyclic voltammograms, the curves in the case of X=0 are different from the other obtained C.V. curves. This experimental observation focus our attention on the effect, which water content of the etching electrolyte, has on the PL process.

3.2. Scanning Electron Microscopy

Scanning electron microscope (SEM) micrographs of the prepared PS samples are shown in Fig. (4). The PS layers are island-like with different dimensions dependent on the etchant type.

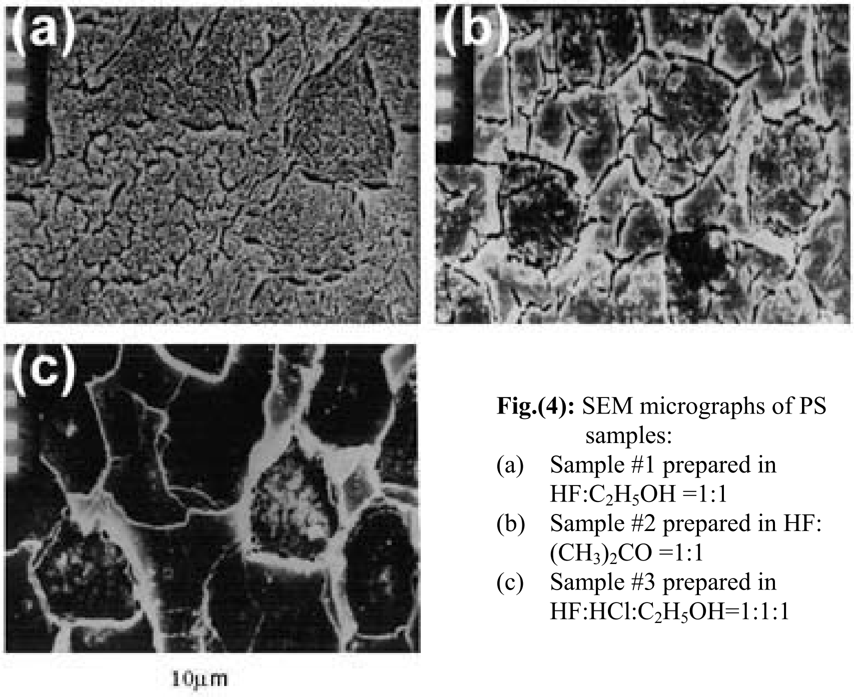


Fig.(4): SEM micrographs of PS samples:
(a) Sample #1 prepared in $HF:C_2H_5OH = 1:1$
(b) Sample #2 prepared in HF: $(CH_3)_2CO = 1:1$
(c) Sample #3 prepared in $HF:HCl:C_2H_5OH = 1:1:1$

3.3. Photoluminescence

The three PS samples fabricated in the three different diluted etchant electrolytes exhibited PL (appeared orange red under ultraviolet (UV) lamp) immediately upon completion of etching, either before drying or after rinsing and drying.

Also, different groups of PS samples were fabricated in the three concentrated solutions; sample #1 in HF/C_2H_5OH, sample #2 in $HF/(CH_3)_2CO$, and sample #3 in $HF/HCl/C_2H_5OH$. Each group of these PS samples was post electrochemical etch treated as is follow:

3.3a. The freshly etched samples and the rinsing process.

Upon the removal from the etching solution, the freshly etched samples coated with the etching solution were PL tested in air. It was found that sample #1 did not give PL immediately but after a gestation period of about 3 min, Fig.(5a), PL started to appear. For sample #2, the gestation period was approximately 90 min Fig.(5b). The sample etched in $HF/HCl/C_2H_5OH$ (sample #3) did not show any PL for any extended period of time.

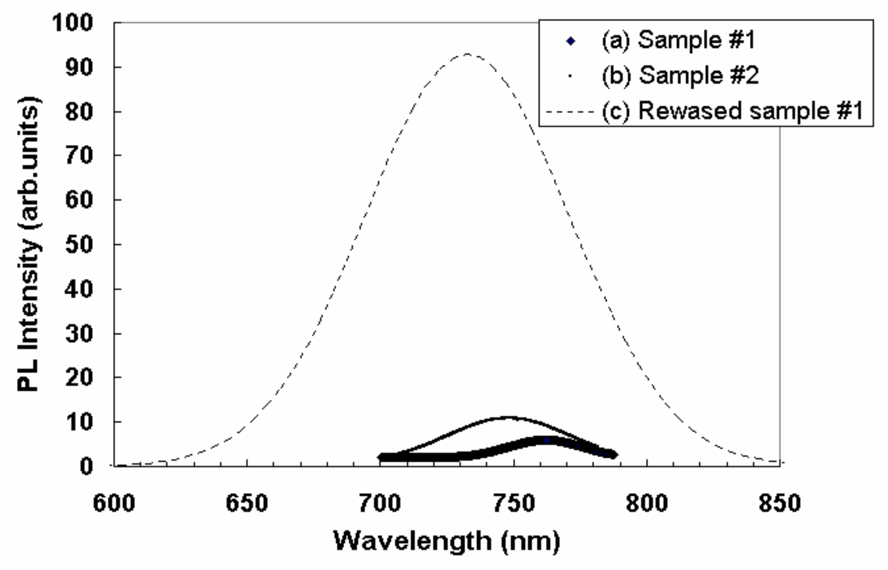


Fig.(5): PL spectra from different samples:
(a) Sample #1 (coated with the etchant electrolyte) after ≈ 3 min from the termination of the anodization current. Intensity is multiplied by 4.
(b) Sample #2 (coated with the etchant electrolyte) after ≈ 90 min from the termination of the anodization current. Intensity is multiplied by 4.
(c) Spectrum obtained immediately after rewashing the previously ethanol rinsed sample(#1) with a mixture of HF & H_2O.

Also, when a drop of water falls on the surfaces of these freshly etched samples coated with the etching solution, the PL was initiated immediately. Moreover, when water was allowed to creep on the surfaces of these freshly etched samples, the PL crept with water simultaneously. When the freshly etched samples were immediately rinsed with ethanol (sample #1 and #3) or acetone (sample #2) then left to dry in air, the three samples started to exhibit PL after a gestation period of about 1 min. When these cleaned samples were rewashed with water, and left to dry in air, the PL intensity did not show any change on the time scale of several days. This behavior is completely different from rinsing the freshly prepared samples with water, giving water a chance to mix with HF on the surfaces of the samples. When the ethanol rinsed samples (#1) were rewashed with a mixture of HF and H_2O, an abrupt increase in PL intensity was observed immediately Fig.(5c); a result which confirmed our suggestion of the combined effect of HF and water mixture.

3.3b. Soaking in the etchant electrolyte.

At the end of the etching process, each sample continued to soak in its HF solution of formation. The PL test was done while the wafer residing continuously in the electrolyte. Visible PL was observed from the sample #1 after 3 hrs soaking (λ_{max}=755nm) followed by a collapse in the PL intensity till a complete quenching of it at about 24 hrs later. Sample #2 gave PL after 1.1 hr (λ_{max}=738 nm) and the PL was completely quenched after 48 hrs. The sample #3 exhibited PL after a gestation period of about 50 min soaking (λ_{max}=690 nm) and its PL was completely quenched after about 9 days of soaking. The PL, of sample #3, started red yellowish (λ_{max}=690 nm) for about 4 days transforming to deep orange with tinges of green till the complete quenching.

3.3c. Soaking in Ethanol, Acetone or HCl/Ethanol.

At the end of the etching process, sample #1 was rinsed with ethanol and soaked in it. It showed a faint PL after about one hour soaking (λ_{max}=770 nm). This PL intensity seems not to change with time. Even rewashing the sample with H_2O did not much affect the PL intensity. On the contrary rewashing with H_2O:HF (1:1), greatly increased the PL intensity. Sample #2 was rinsed and soaked in acetone. The PL was observed after about one hour soaking and enhanced with the course of soaking time (λ_{max}=755 nm). Then it seemed stabilized to about two times increase in PL intensity at about one day of soaking. Two samples from type #3 were used. The first was rinsed with ethanol and soaked in it. It developed PL after about one hour (λ_{max}=705 nm); exactly the time of sample#1. So, It seemed that the behavior of the PL in ethanol was quite similar regardless of the manner in which the sample was prepared. The second type #3 sample was rinsed with ethanol and soaked in HCl/ethanol (1:1). In that case, very strong PL was on after about one min from soaking and the intensity was five times higher than the initial value. Moreover, taking the sample out of the solution did not affect this strong PL intensity.

4. Discussion:

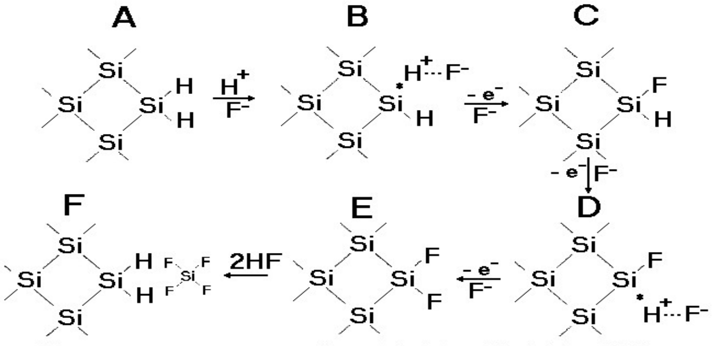
4.1. Etching and the Photoluminescence Process.

The dissolution of Si in an HF-containing electrolyte was discussed by many authors [13,14]. Also, Dudel et al. [15] suggested the formation of a silicon hydroxide (Si-OH) bond and the creation of a surface bound silicon oxyhydride to be essential to the luminescence process. The formation of the silicon oxyhydride emitter appears to be consistent with the comparative and competitive mechanisms, previously suggested for silicon dissolution in aqueous and nonaqueous media [13,14]. Fig.(6a) outlines the cycle of the suggested conversion steps in a nonaqueous etching process that provides the dissolution of silicon through the eventual formation of a SiF_4 leaving group.

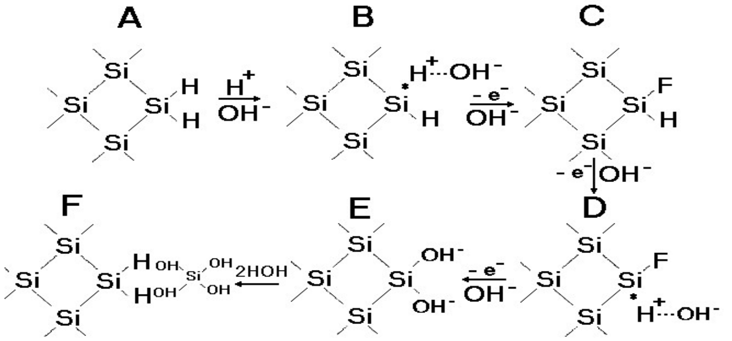
This process [13] in HF/MeCN solution is thought to form an initial dihydride surface (A) and is confirmed by theoretical calculations [16]. The initially stable dihydride surface does not appear to be photoluminescent [2,3,5,13]. This starting situation (A) represents a kink site of a (111) surface in which the Si atom has two bonds to the silicon lattice and the two remaining bonds are saturated by H ligands. The reaction sequence with HF is thought to be hole initiated (B). The presence of holes at the Si/electrolyte interface enhances the Si-H bond breaking [17], producing a proton and a silicon radical. After electron ejection into the silicon conduction band, facilitated by the ready oxidation of silicon, the positively charged silicon is thought to be complexed by a fluoride ion (C). This process is thought to continue as the high electronegativity of fluoride in the silicon fluoride bond destabilizes the adjacent Si-H bond. This Si-H bond is then more susceptible to oxidation through electron injection or hole consumption (D). A fourth oxidative step (E) through electron injection can take place as the addition of fluoride to the oxidized silicon further destabilizes the Si-Si bonds. The polarity of the Si-F bonds can facilitate the further addition of HF and the final dissolution of SiF_4 that dissolves as the silicon hexafluoride.

Many authors [14,15] outlined that the presence of water in the etch solution inhibits the anhydrous dissolution process. Water competes effectively with fluoride in complexing silicon resulting in less reactive intermediates because of the lower electronegativity of hydroxide as compared to fluoride. The competitive mechanism indicated in Fig.(6b) is thought to proceed through the formation of silicon hydroxide bonds, which can result in surface bound photoluminescent oxyhydrides [2,5]. It was suggested [7], that water can interact in- at least- three different ways with a silicon surface to produce Si=O, Si-O-Si, and Si-OH bonding units.

Taking into consideration the suggested mechanism for the steady-state oxidation of the hydrogen–coated silicon surface in an aqueous electrolyte (Fig.6b), the hydrolysis of silicon (B,C) can compete favorably with fluorination, as oxide bonds are readily formed during silicon anodization [13,14]. The hydrolysis of the silicon radical (B) represents an important alternate oxidation route as water can lead to the formation of an Si-OH bond, which is a form of oxyhydride, with a noncompletely hydride decorated silicon surface considering the possible formation of the other bonding units Si=O or Si-O-Si bond through a water molecule reaction with silicon surface, i.e. the combination of water reactions produce an-Si(O)(OH) or-$Si(O)-(OSiH_3)$ oxyhydride fluorophor. The formation of the hydroxide bond alters and decreases the reactivity of the remaining Si-H bond (C), which is now less susceptible to electron injection or nucleophilic attack. The lower induced polarization of the hydroxide group also weakens the Si-Si bonds to a lesser extent, signaling an increased stability for the hydroxy intermediates indicated in C and E. Water can lead to the formation of silicon oxide and hydroxide bonds in comparison with silicon fluoride bond. This results in the creation of silicon oxyhydride surface entities, leading to stable surface product. This could be the reason that the pure water/HF solution gives the maximum peak height compared to other etchants used in C.V. [Also, the increase of the current peak height with the increase of the water content of the electrolyte could be attributed to the increase of the electrolyte conductivity resulting from the electrolyte dilution]. It seems that, in aqueous etching solution, the competitive branching between hydroxide and fluoride formation is in large part responsible for the formation of photoluminescent emitters in direct competition with dissolution and SiO_2 formation [18].



Non-aqueous etch of Si in HF-MeCN.



Aqueous etch of Si in HF-H2O-M.

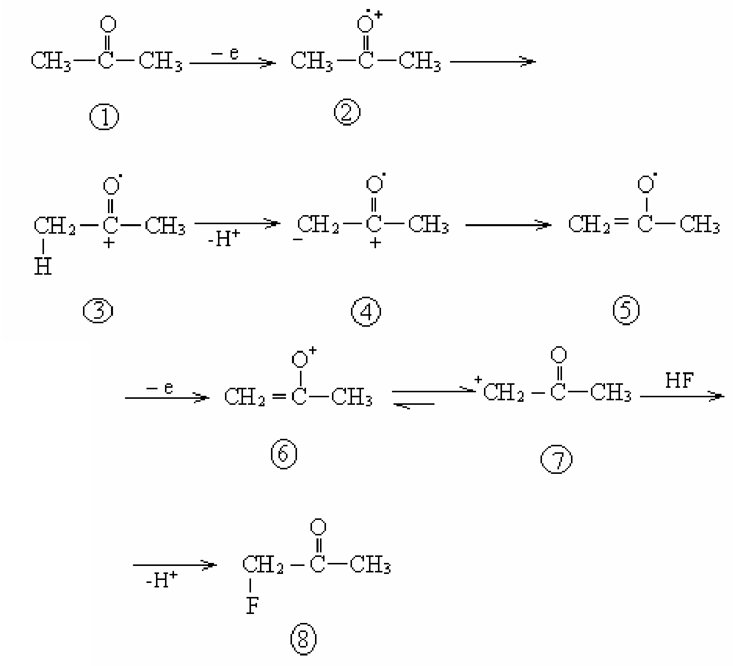
Fig.(6): Reaction mechanisms for dissolution and silicon fluoride and silicon hydroxide (oxyhydride) bond formation in nonaqueous and aqueous HF etch solutions.

Similarly, the presence of C_2H_5OH in the etchant can alter the etching cycle through direct reaction or possibly through production of constituencies such as C_2H_5F i.e.,

$$HF + C_2H_5OH \rightarrow H_2O + C_2H_5F$$

which can rapidly react with the silicon surface [7].

Also, when acetone is present in the etchant solution during the anodization process, the observation of PL may be rationalized in terms of the following scheme:



According to such a scheme, we proposed that acetone undergoes anodic oxidation to give the radical of the respective enol form (5), which then undergoes further oxidation to yield the cation (6). This latter is attached by HF to give fluoroacetone (8), which react with the silicon surface resulting in the PL phenomenon. This reaction is slow and needs time for its completion, which may explain the initial lower degree of PL intensity with its progressive growing in case of soaking sample #2 in acetone. The PL gets its final maximum value when a complete blocking of Si wafer surface, for further fluoroacetone attack, is reached.

On using HF/HCl/C_2H_5OH for the electrochemical etching of silicon, HF is partially ionized to H^+ and F^-, while the HCl acid is almost completely ionized in water producing (H^+) and (Cl^-) ions. The increase in (H^+) concentration significantly decrease the (OH^-) concentration in solution since $[OH^-] = K_{water}/[H^+]$. Kim et al. [19] demonstrated that increasing the H^+ concentration resulted in support of emitter quality on the PS surface. Also, it was mentioned that the introduction of NaOH to postetch weakly acidic solution completely quenches the PL as it lowers the H^+ concentration relative to that associated with the water, $H^+ + OH^-$ equilibrium. The HF acid interacts with the decorated silicon surface to remove a portion of the PL emitters. In addition, because of the lower electronegativity of the chloride as compared to fluoride, the (Cl^-) ion also can have a stabilizing effect as the stability of the SiCl bond is notably weaker [14,20] than that of the Si-F, Si-$OSiH_3$ or Si-OH bonds on the oxidized PS surface. The (Cl^-) ion will be less likely than (F^-) to remove or compete with hydroxide bond formation and for this reason, serves to maintain and stabilize the silicon oxyhydride surface entities [21]. So, the increase in the H^+ and Cl^- concentration directly related to the enhanced PL behavior [21].

4.2 j-v. Characterization of Si in 1% HF solution:

The general shape of the voltammograms reported in the present work consists of two current maxima and an electropolishing plateau beyond the second peak. The first peak marks the transition from PS growth to electropolishing and the second one appears to be related to a transition from an –OH-terminated surface to oxide growth [22,23]. The first peak is commonly called the critical current peak, j_{crit}. The potential and magnitude of j_{crit} are dependent upon solution pH, agitation, doping density, HF concentration, crystal orientation, and illumination intensity [9,24]. Pore formation occurs only in the initial rising part of the j-v curve for a potential value below the potential of the first peak [25]. At low current densities, the electro-oxidation ultimately results in dissolution of SiF_4 and the reaction of Si with water to produce surface hydroxyl groups is significant. The formation of hydroxyl groups on the surface facilitates the formation of PL centers. The water can react with Si surface through the formation of silicon hydride and siliconhydroxide bonds across adjacent silicon surface atoms (Fig.6) and the concerted reaction of a water molecule at a silicon atom site to form oxide with the subsequent release of hydrogen or the insertion of oxygen into a silicon-silicon surface bond [26]. At $j<j_{crit}$, the rate of silicon dissolution as SiO_2 or $Si(OH)_4$ is very slow, consequently extending the lifetime of the water-based surface oxidation intermediates Si=O, Si-O-Si, and SiOH. As the current density increases, formation of these constituents at the surface increases leading to an increase in PL emission intensity [7]. At potential higher than the first current peak and lower than the second one, a transition zone exists where pore formation and

electropolishing compete for control over the surface morphology [9]. The resulting structure within this region is generally porous in nature and the diameters increase rapidly as the electropolishing potential is approached. At $j > j_{crit}$, the rate of further oxidation of the surface intermediates increases and the rate of dissolution as SiO_2 or $Si(OH)_4$ increases proportionately. This leads to the reduction and eventual quenching of the PL. At anodic overpotentials in excess of the second current peak, silicon electropolishes[25].

An exception of the above mentioned behavior is the case of X=0, In that case, neither a critical current peak nor an electropolishing region was observed in HF/C_2H_5OH or $HF/(CH_3)_2CO$ etchant electrolyte. Also in $HF/HCl/C_2H_5OH$ etchant electrolyte, despite that the j-v relation is not linear; the behavior is not the standard one for PS formation. In this Fig., the presence of current variations at higher applied potential, could be attributed to local fluctuations in the thickness of the surface oxide due to numerous, independent, and self-varying islands of silicon dissolution [24].

At X=0, The water concentrations in the three used electrolytes could be considered as a small one (≈0.4%), and its effect on the C.V. curves seems to be negligible. The other important feature to be noted in the C.V., is the dependence of the current peak height on the composition of the etchant electrolyte. Fig.3 shows that:

$J_{crit}(HF/HCl/C_2H_5OH/H_2O) > J_{crit}(HF/ (CH_3)_2CO /H_2O) > J_{crit}(HF/C_2H_5OH/H_2O)$, [for $x \leq 50\%$]

The increase of the current density results in an increase in the formation of the PL emitter molecules [7]. This was reflected in the PL exhibited by the samples.

4.3 Postetch treatments :

4.3a Freshly etched samples coated with the etchant and rinsing.

Two of the freshly etched samples (sample #1 and sample #2) coated with the etchant give PL after a gestation period of about 3 min.

The growth of the PL with time for this gestation period suggests the initiation of electroless chemical reaction resulting in a growth of the PL emitters (silicon oxyhydride) to cover the whole PS surface. It was reported [15] that the electrochemical etching process both creates and destroys PL emitters. Similarly, this could be suggested here and the reaction proceeds to the formation of the PL emitters as their formation exceeds the dissolution. Then the reaction is stopped due to the completion of the drying process for some etchant components. With respect to sample #3, which gave no PL, it seems that the presence of HF/HCl/C_2H_5OH induces structural changes in the surface molecular emitters resulting in a complete disappearance of the PL.

Also, we found that, wetting the sample surface (for sample #1 and #3) with one water drop in the presence of HF or the etchant electrolyte leads to PL initiation. It seems that the water content of the concentrated etchant electrolyte is not sufficient to initiate the reaction for formation of the PL emitter (silicon oxyhydride). Enough water completes the oxyhydride formation leading to the initiation and enhancement of PL.

In case of ethanol rinsing (sample #1 and #3) or acetone rinsing (sample #2), followed by air-drying, the PL was initiated from the three samples after a gestation period of about 1 min. Rewashing these cleaned samples with water did not alter the PL intensity. This situation looks completely different from the effect of rinsing or wetting the freshly prepared PS sample with water (giving water a chance to mix HF on the PS surface). We observed that, if the freshly prepared sample is rinsed with water it exhibits a considerable stronger initial PL than does a freshly prepared sample cleaned with ethanol or acetone before rewashing it with water, so fluoride is proposed to act as a catalyst loads the surface with silicon oxyhydride.

4.3b. Soaking the PS samples:

The PL features studied for PS samples soaked in the etchant solution after the end of the etching current (i.e. the initiation of the PL after a gestation period followed by a complete quenching of the PL) are different from those features studied for PS samples coated with the etching solution in air. It seems that in air and in the presence of ethanol (sample #1 and sample #3) or acetone (sample #2), the water can be leached from the pores and the drying process is hastened for some etchant components. The results show that the PL properties of the PS samples depend on the specific constituency of the etching solution and the condition under which the PL from PS is measured. This behavior may be the result of surface changes with time due to electroless chemical changes.

The PL behavior of sample #3, soaked in (HCl/ethanol/HF) looks more interesting. This behavior favors a chemical transformation process involving two distinct surface species [7]. The PL color changes seem to be distinct surface entities, which are selectively excited by the UV light source. So soaking the PS samples in (HCl/ethanol/HF) electrolyte could be used to get different wavelengths PL emitters. The stabilization of these different color emitters needs more investigations. The PL initiation and quenching after a notable gestation period following the end of the electrochemical etching process and while the sample is left soaking in the etchant electrolyte, could be explained by considering that the etchant electrolyte might interact differently at distinctly different times in the postetch treatment process. At the beginning of the process, the reaction proceeds to the formation of the PL emitters till the complete surface coverage of the PL emitters as their formation exceeds the dissolution. Whereas after the complete surface coverage of the PL emitters, the dissolution process exceeds the formation till the complete quenching of the PL. When the samples were rinsed and soaked in ethanol (sample #1 and sample #3) or acetone (sample #2), the three samples exhibit PL after 1 hr soaking. The PL intensities of the sample #1 and #3 did not change with the soaking time while the PL from sample #2 grew more intense with time reaching a maximum at about one day i.e. some reactions are slowly growing which is in consistent with the proposed interaction mechanisms of acetone with HF on the silicon surface mentioned in section 4-1.The PL from the three samples did not quench for about 2 weeks. So the presence of the HF in the postetch solution leads to the quenching of the PL.

5. Conclusions:

The j-v relation shows that, up to ≈ 50% water in the etchant electrolyte: J_{crit} (HF/HCl/C_2H_5OH/H_2O)> J_{crit}(HF/ $(CH_3)_2CO$ /H_2O) >J_{crit}(HF/C_2H_5OH/H_2O).

Also, the j-v relation in case of concentrated electrolytes (≈0.4 % water) is not the standard one for PS formation. These results are reflected in the PL properties of the fabricated PS samples. Porous silicon samples fabricated via anodization in concentrated electrolytes show a PL after a gestation period. Water in the presence of HF has a pronounced influence in the PL intensity of these concentrated samples. Soaking the porous silicon samples in their HF solution of anodization, results in an initiation of PL after a gestation period followed by a PL collapse till a complete PL quenching. On the contrary, soaking in HF free solution of anodization results in an initiation of PL after a gestation period without an intensity collapse.

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References:

1. L.T.Canham, *Appl. Phys. Lett.*, **57** (1990) 1046

2. J.L.Gole, F.P.Dudel, D.Grantier, and D.A.Dixon, *Phys. Rev*. **B56**, 2137 (1997)

3. J.L.Gole, and D.A.Dixon, *Phys.Rev*.**B57**, 12002 (1998)

4. J.L.Gole, and D.A.Dixon, *J.Phys.Chem*.**82,** 3125 (1997)

5. J.L.Gole, and D.A.Dixon, *J.Phys.Chem*.**102**, 33 (1998)

6. Chi-Huei, Si-Chen Lee and Yang-Fang Chen, *J.Appl.Phys*.**75**, 7728 (1994)

7. J.L.Gole, F.P.Dudel, L.Seals, M.Reiger, P.Kohl, and L.A.Bottomley, *J.Electrochem. Soc*. **145**, 3284 (1998)

8. B.R.Dzhumaev, *Semiconductors*, **33**, 11, 1379_ (1999)

9. X.G.Zhang, S.D.Collins, and R.L.Smith, *J.Electrochem. Soc*. **136**, 1561 (1989)

10. Halimaoui, in Porous Silicon Science and Technology, edited by J.-C.Vial and J.Derrien p.33, Springer, Berlin (1955),

11. M.Bailes, S.Bohm, L.M.Peter, D.J.Riley, and R.Greef, *Electrochim.Acta*, **43**, 1757 (1998).

12. C.daFonseca, F.Ozanam and J.N.Chazalviel, *Surf. Sci*. **365**, 1(1994).

13. E.K.Prpst, and P.A.Kohl, *J.Electrochem.Soc*. **141**, 1006 (1994)

14. H.Gerischer, P.Allongue, and C.Kieling, *Ber. Bunsenges. Phys. Chem*., **97**, 753 (1993)

15. F.P.Dudel, and J.L.Gole, *J.Appl.Phys*.**82**, 402 (1997)

16. G.W.Trucks, K.Raghavachari, G.S.Higashi, and Y.J.Chabal, *Phys. Rev. Lett*., **65**, 504 (1990)

17. H.Gerischer and W.Mindt, *Electrochim.Acta* **13**, 1329 (1968)

18. J.L.Gole, and D.A.Dixon, *J.Phys.Chem*.**B102**, 1768 (1998)

19. K.-J.Kim, H.-S.Park, T.-S.Kang, and H.-G.Lee, in 194th Meeting of *Electrochemical Society*, Boston, 1998,98-2, Abstract No.769(1998)

20. A.G. Gaydon, "*Dissociation Energies of Diatomic Molecules*"; Chapman and Hall Ltd.: London(1968) Chap.12

21. J.L.Gole, J.A.DeVincentis, L.Seals, P.T.Lillehei, S.M.Prokes and D.A.Dixon, *Phys.Rev*.**B61**, 5612 (2000)

22. F.Ozanam and J.N.Chazalviel, *J.Electron.Spectrosc*.**64/65**, 395 (1993).

23. Reference 23 p.29 and references therein.

24. R.L.Smith, and S.D.Collins, *J.Appl.Phys*.**71**, R1 (1992)

25. S.Cattarin, L.M.Peter, and D.J.Riley, *J.Phys.Chem*.**B.101**, 4071 (1997)

26. S.B.Oblath and J.L.Gole, *J.Chem.Phys*.,**70**, 581 (1979)