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BEHAVIOUR OF PLASMA HYDROGENATED n-TYPE SILICON IN AQUEOUS FLUORIDE MEDIA

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Abstract

In this paper we have investigated the electrochemical behaviour, in the dark, of hydrogenated n-type silicon (n-Si (H)) as function of the plasma hydrogenation duration. We also study the pore size microstructures and the flat band potential V_{fb}. The results are compared with non-hydrogenated n-Si. To explain thisresults we had proposed electro- chemical reactionary mechanism, in which one of the species created by the plasma accelerates the oxidation of the silicon even at anodic polarisation.

This reaction is $SiH_2 + 2F^-_{att} \Rightarrow SiF_2 + 2e^- + H_2$ through it two electrons are injected in the conduction band. Then we had concluded that the mass loss and porous material formation is seriously affected by the hydrogenation.

Keywords: *Porous silicon; Plasma hydrogenation; Electrochemistry; Dark current, capacitance-voltage; Surface morphology.*

Résumé

Dans cet article, nous avons étudié le comportement électrochimique, dans l'obscurité, du silicium de type n hydrogéné n-Si (H)) en fonction de la durée d'hydrogénation du plasma. Nous étudions également la microstructures de taille de pore et le potentiel de bande plate V_{fb}. Les résultats sont comparés au Silicium de même type non hydrogéné. Pour expliquer ces résultats, nous avons proposé un mécanisme réactionnaire électrochimique, dans lequel une des espèces créée par le plasma, accélère l'oxydation du silicium même sous polarisation anodique.

Cette réaction est $SiH_2 + 2F^-_{att} \Rightarrow SiF_2 + 2e^- + H_2$ où deux électrons sont injectés dans la bande de conduction. Nous avions conclu que la perte de masse et la formation silicium poreux est sérieusement affectée par l'hydrogénation.

Mots clés: *Silicium poreux; Hydrogénation du plasma; Electrochimie; Courant à l'obscurité; Capacité différentielle; Morphologie de surface.*

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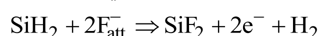
ملخص

في هذا الإطار قمنا بالدراسة الكهركيمياوية للسلسيوم من نوع n المهدرج ببلاسمة الهيدرجين .لقد كانت الدراسة بدلالة زمن الهدرجة اما طبيعة الدراسة فكانت تحت شروط الظلام حيث تطرقنا في هذا البحث إلى البنية المجهرية لسطح العينات بعد تعرضها لعملية النقل الكهربائ عبر السطح، وكذلك كمون العصابة المستوية أي V_{fb} وطبيعة الإزاحة لهذه الأخيرة. قورنت هذه النتائج مع نظيرتها للسليسيوم غير المهدرج (اي غير المعالج)؛ فلقد تم إقتراح آلية تفاعل كهركيميائ والذي من خلاله شرحنا عملية تسريع أكسدة السيلسيوم رغم الإستقطاب العكسي له والذي عادة لا يأدي الى أكسدته. هذا التفاعل كان على المنوال التالي:



$$SiH_2 + 2F^-_{att} \Rightarrow SiF_2 + 2e^- + H_2$$

من خلال هذا التفاعل تجري عملية حقن إلكترونين في عصابة النقل لتضمن التنقل الجزئ للإلكترونات وبالتالي الأكسدة؛ فيحدث عن ذلك التأكل للمادة والتقعر لها.

الكلمات المفتاحية: تقعر Si، هدرجة Si، كهروكيميا، التيار المظلم، السعة-التيار، الشكل السطحي.

Silicon in contact with HF as an electrochemical system has always been used in microelectronic technology. The importance of clean substrate in fabrication of semiconductor microelectronic devices has been recognized since the early days of the 1950s; scientific focus on these substrates started only lately after it was shown that various porous layers with dimensions scaling from nanometers to micrometers can be obtained easily [1,2].

The earlier studies are those in which the dissolution of silicon took place. In this context Memming and Schwandt [3] have suggested a number of subsequent chemical and electrochemical disproportionate reactions in which the unstable SiF_2 species is transformed into tetravalent H_2SiF_6 and molecular hydrogen; whereas at electro polishing potentials, silicon is thought to dissolve directly in the tetravalent state [3,4]. Later it was shown that by increasing the potential from the rest potential, the divalent dissolution appears and undergoes the porous silicon formation but at higher anodic potential, the electro polishing region is reached; silicon undergoes a tetravalent dissolution [5,6].

Other studies have been carried out [7-10] in which the morphology of porous silicon have been studied as function of crystal orientation, doping concentration, potential, and hydrofluoric acid concentration. The work of Chazelviel *et al*. [11-13] showed that the magnitude of the currents is affected by the concentration of various fluoride species, mainly F^-, HF, HF_2^- and H^+; also by the salt cations at lower pH.

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Recently it is well known that silicon surfaces are terminated by hydrogen after chemical etching in buffered HF solution. Although hydrogen terminated silicon surfaces have been extensively studied but there are few reports about the behaviour of treated surface silicon. The except studies are those published by de Mierry *et al.* [14] and Allongue *et al.* [15] in which the authors incorporated hydrogen in silicon by electrochemical methods also few studies have been carried out [16] in which the role of hydrogen in the formation of porous structures has been investigated.

In this paper we investigate the effect of plasma hydrogenation for different period of treatment. We present a comparative electrochemical study of the hydrogenated and non hydrogenated n-type silicon. The pore of n-hydrogenated silicon microstructures and the flat band potential V_{fb}(H) after hydrogenation are briefly discussed.

Both dark current-voltage and capacitance-voltage are used here as electrical measurements and (S.E.M) is used to observe the topographical surfaces of the samples after the measurements.

An electrochemical reactionary mechanism is proposed to explain the results; in which one of the species created by the plasma accelerates the oxidation of the silicon even at anodic polarisation under dark condition.

EXPERIMENTAL

The samples used in this study were n-type silicon single crystals, phosphors doped ($3.10^{15}cm^{-3}$) with <111> orientation. Their hydrogenation was performed by a plasma of hydrogen under the following conditions: 398 K, 1mb H_2 for three periods of time (15, 30, and 60 min) at 20 Watts.

The ohmic contact was performed on the backside of the samples surfaces by depositing Ga-In alloy. Then the sample was fixed to a copper sheet with silver paste. A Sample and a copper sheet were mounted at the bottom of the cylindrical electrolysis cell, made of Teflon .The part of the sample in contact with the solution, is the working electrode. The counter electrode was a platinum sheet (1mm x 5mm). The reference electrode was a saturated calomel electrode (SCE) which was connected to the cell solution via KCl filled bridge made of Teflon. The solution was made from 48% HF, distilled water and NH_4Cl as support salt. The formal fluoride concentration, C_f was 0.03 M. Prior to testing, each non-hydrogenated sample was degreased with solution of $16HNO_3+3CH_3COOH+1HF$ in volume proportion for 4 min and rinsed in distilled water, then dipped in 48% HF for 1min to remove oxide from the surface and leave a H termination. The hydrogenated sample was used directly after the plasma treatment.

To return to the non hydrogenated initial state, two methods were applied here in:

-the first one is the chemical etching of the hydrogenated layer. It was accomplished in acidic solution of $10HNO_3 + 3CH_3COOH + 1HF$ in volume.

-the second one is the out-diffusion of hydrogen from the bulk of the samples; it was performed by annealing at 673 K for one hour, under a vacuum of 4.10^{-6} Torr as mentioned in ref. [17,18]. This method lets the surface of the samples H terminated.

RESULTS AND DISCUSSION

It is well known from the literature [19-24] that the porosity of silicon during its dissolution in HF is between 10 and 80 %. The pore size and the porosity depend upon the working conditions (substrate characteristics, current density, hydrofluoric solutions, ...) and the pore size is in the range (1nm to 1µm). The pores are separated by very small size silicon columns. This reflects a selective reactivity of the electrode surface.

Chazalviel *et al.* [11] explained the increasing current density, lying between the two electro polishing plateaux by setting off localised corrosion on the electrode surface.

Figure 1 shows the dark current-potential curves for a non-hydrogenated n-Si sample and three samples hydrogenated for three different periods of time (15 min, 30 min and 60 min). A weaker anodic current is observed for the non-hydrogenated sample see (Fig. 1a); it was explained by the injection of electrons into the conduction band either in fluoride solutions [25] or NaOH solutions [26].

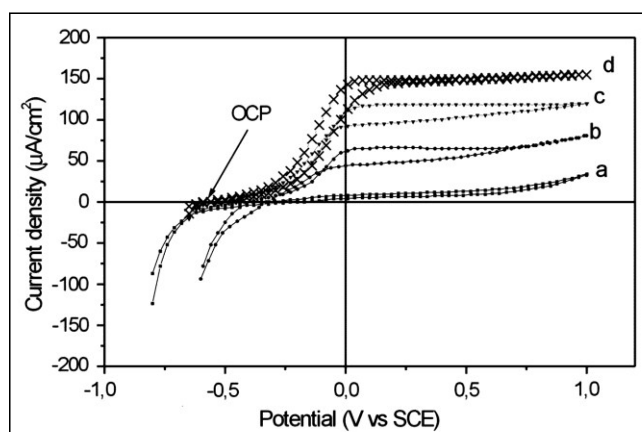

Figure 1: Voltammograms of n-Si/HF in the dark C_F = 0.03M NH_4Cl = 1M. **(a)** non hydrogenated sample, **(b)** sample hydrogenated for 15 min, **(c)** sample hydrogenated for 30 min, **(d)** sample hydrogenated for 60 min.

One sees for all treatments a shift of the open-circuit potential (OCP) in the negative direction, increasing with hydrogenation time. The Tafel slopes for the *I-E* curves are between (-0.45) and (0.05 V_{SCE}) and are very distinct in the case of samples treated for 30 min and 60 min; the slopes have parallel shift with time interval as it is shown in figure 2. From the parallel shift of the Tafel slope one can deduce that the oxidation reaction, implied here, has the same charge transfer coefficient. Whereas the extrapolation of the slope to the origin of the potential indicates that the concentration of the reactants species is not the same at the surface samples. When the potential increases, the current reaches a constant value. Fig. 1(d) shows the order of magnitude, which is about 150 $\mu A.cm^{-2}$ in the case of the sample hydrogenated for 60 min. It reflects a permanent dissolution of the species induced on the surface by the plasma treatment. Between the Tafel region and the saturation current there is a transition region.

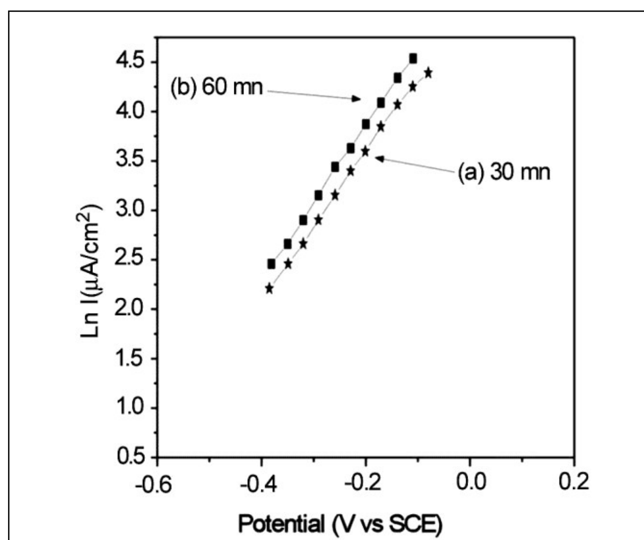

Figure 2: Logarithmic current density vs. potential curves in the region of porous silicon formation. **(a)** sample hydrogenated for 30 min, **(b)** sample hydrogenated for 60 min.

In order to know the origin of the observed effect (i.e., the increase of the current), if it is due to hydrogen or just to disorder induced by plasma, we focused on the returning to the initial state (non-hydrogenated surface) by using two different ways as described in the experimental part.

After the chemical etching of the hydrogenated layer, we can see (Fig.3b) that not only the return of the anodic currents to smaller values but the shift of the (OCP) in the positive direction also, exactly as in the non-hydrogenated sample (initial state). The same behaviour is shown in Fig. 3c after the out-diffusion of hydrogen from the bulk sample.

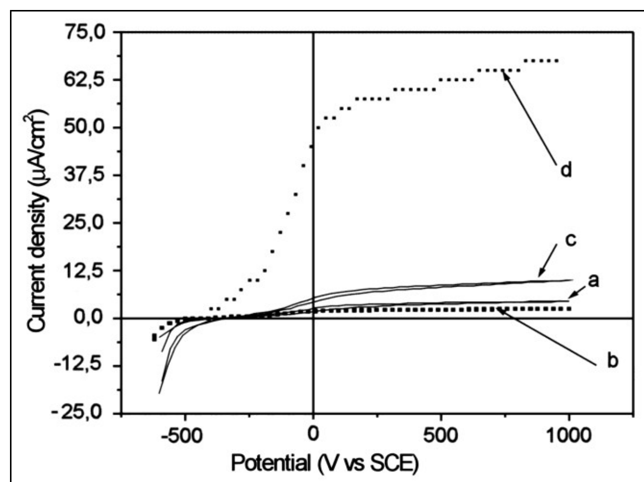

Figure 3: Voltammograms of n-Si/HF in the dark C_F=0.03M NH_4Cl=1 M. **(a)** non hydrogenated sample, **(b)** etched sample, **(c)** out-diffused sample, **(d)** sample hydrogenated for 15 min.

This behaviour allows us to think that the increasing current and the (OCP) shift are linked to the incorporated quantities of hydrogen; since the quantities of hydrogen are related to the time interval treatment.

A topographical study of the samples by (S.E.M) shows that the pore-size, after the same number of polarisation

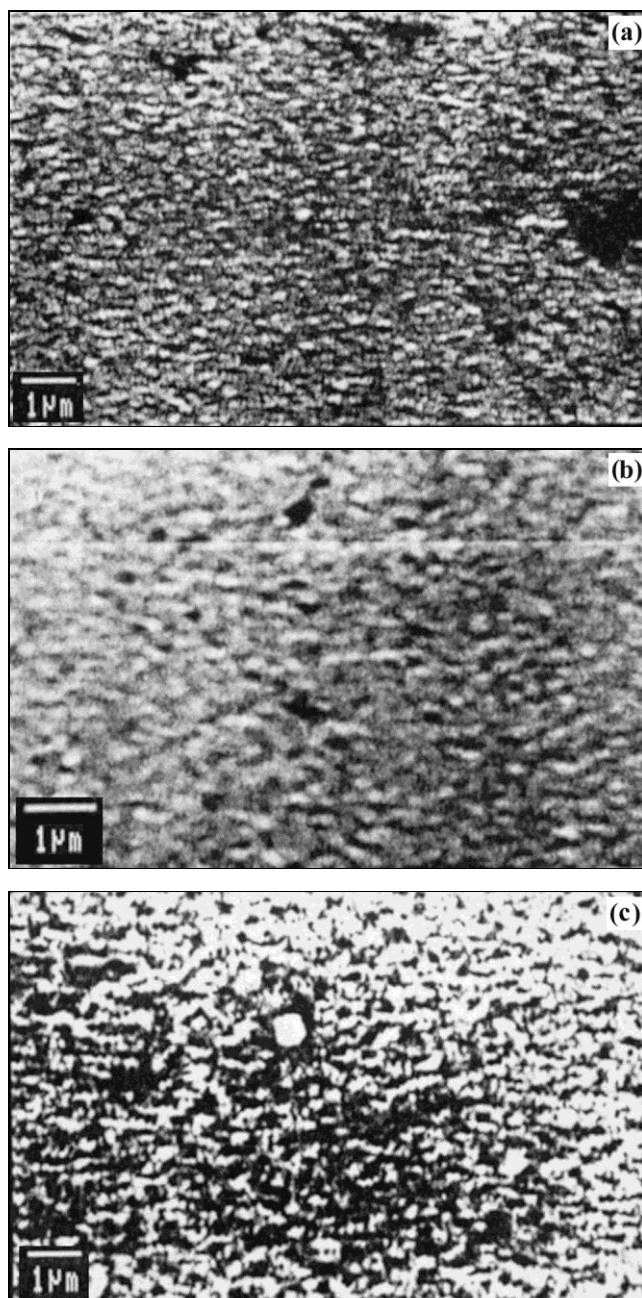

Figure 4: Surface morphology of n-type silicon after the same number of cycles under a weak illumination.
(a) sample hydrogenated for 15 min,
(b) sample hydrogenated for 30 min,
(c) sample hydrogenated for 60 min.

cycles, increases with hydrogenation period of time; the evolution of the surface morphology is shown in figure 4. It is clear that the mass loss of the substrate depends upon the hydrogenation period of time. This porosity is preserved even at high potentials which may be due to the permanent dissolution of the species involving silicon, induced by plasma, in hydrogenated n-silicon samples. These results are quite consistent with those reported by Allongue et al [15]. In the same work the authors observe not only a selective etching in fluoride solutions but a formation of a macro porous silicon layer in n-type as well in regions highly disordered by H-induced micro defects.

The C^{-2}-E curves are plotted according to the Mott-Schottky (M-S) relation, which is described elsewhere, just after the dark current measurement.

For each duration of treatment, figure 5 shows that both the flat band potential $V_{fb}(H)$ and M-S slopes of the curves change. A negative shift of the $V_{fb}(H)$ is observed which increased with the time of hydrogenation which is in agreement with the observation of Allongue et al [15]. $V_{fb}(H)$ value is less than (-1.3 V_{SCE}) in the case of the sample treated sixty minutes. This value leads us to consider it as an apparent value $V_{fb}(H)_{app}$ since the corresponding energy is larger than the band gap of Silicon.

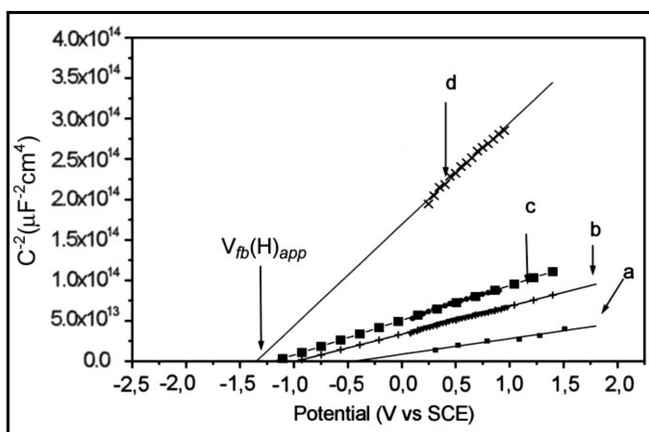

Figure 5: Mott-Schottky plots for n-Si/HF in the presence of 1M NH_4Cl and C_F=0.03M. **(a)** non hydrogenated sample, **(b)** sample hydrogenated for 15 min, **(c)** sample hydrogenated for 30 min, **(d)** sample hydrogenated for 60 min.

These results indicate that both the surface and the bulk were modified by the time of the treatment (i.e., the quantities of hydrogen incorporated in silicon) since both the etching of the hydrogenated layer and the out-diffusion of hydrogen from the sample give a good confirmation of $V_{fb}(H)_{app}$ shift and the change in M-S slope of the curves. It was shown in figure 6, the disappearance of the two behaviours and the return to the initial state (steady state).

These behaviours may be understood as follows: $V_{fb}(H)_{app}$ shift can be related to an excess of (H^-) at the subsurface of the sample and M-S slope change may be related to the gradual passivity of donors in the bulk of silicon by formation of neutral H-Si-P complexes [27].

In this study, the samples were hydrogenated, so their surfaces are different to the non-hydrogenated one. They react differently towards the solution; In fact it was shown in figure 4, curves (a), (b), (c), that after the same number of polarisation cycles the evolution of the surface morphology depends on the hydrogenation period of time. The same observation was reported in ref. [14] but the hydrogen is incorporated by electrolytic method.

Before starting the discussion about the origin of the increasing dark current and $V_{fb}(H)_{app}$ shift to more negative potential in the hydrogenated samples, it is necessary to give a summary of hydrogen diffusion behaviour in silicon and also its charge state: hydrogen plasma diffusion in silicon is known to introduce different species which are

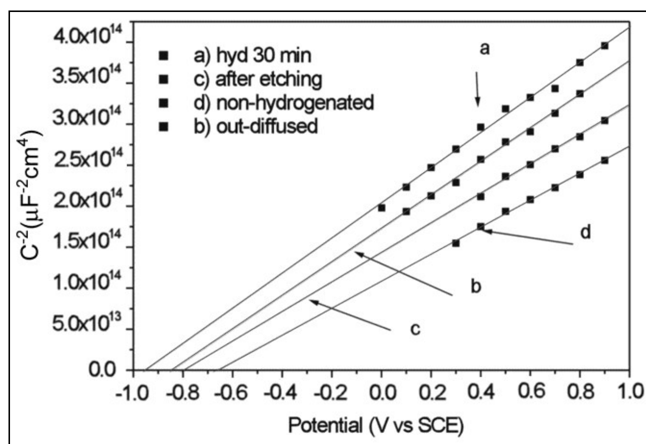

Figure 6: Mott-Schottky plots for n-Si/HF in the presence of 1M NH_4Cl and C_F=0.03M.**(a)** hydrogenated sample for 30 min, **(b)** out-diffused sample, **(c)** etched sample (after hydrogenation), **(d)** non hydrogenated.

differently charged such as H_2, H^0, H^+ and H^- . These species diffuse into different depths with different diffusion coefficients (D_H^*). The diffusion depends on the specie size and charge state and also on the nature and the level of doping and the conditions of the plasma annealing treatment (time and temperature). In both cases of n-type Si and p-type Si, SIMS profiles exhibit an excess of hydrogen, at the half diffusion deep. Concerning the charge state of diffusing hydrogen, it depends on the type of silicon as follows:

1°) in hydrogenated p-type Si, hydrogen is predominantly present as H^+. Its diffusion is related to the sample temperature and doping condition. H^+ diffuses rapidly (even at room temperature) and drifts in the electric field set up in the near surface region of the Si substrate [19,20]. A great amount of this specie will neutralise the ionised acceptors by forming neutral complexes. Molecule formation occurs through hydrogen association reaction such as:

$$H^0 + H^0 \rightarrow H_2 \quad \text{and} \quad H^0 + H^+ \rightarrow H_2 + h^+ .$$

where h^+ is a hole.

2°) in hydrogenated n-type Si there is a mixture of H^- and H^0 . Their diffusion depends on the doping density and the sample temperature. The two species move more slowly in n-type Si than the H^+ in p-type Si. At low temperature (< 150°C), H^- neutralises the ionised donors by forming neutral complexes and drifts in the electric field set up in the near surface region of the silicon [27]. Molecule formation occurs through hydrogen association reaction such as:

$$H^0 + H^0 \rightarrow H_2 \quad \text{and} \quad H^0 + H^- \rightarrow H_2 + e^-$$

The molecules (H_2), which are formed through hydrogen association, are much less mobile than the atomic species. The neutralisation of the donors, which is more than 60 % [27], is weaker than the neutralisation observed with the acceptors, which is 99 % [19, 20]. The excess of hydrogen over the donors concentration may be present as H^- which was confined at the subsurface layer of the silicon substrate.

A part the confined species, charged negatively, participate in the formation of a subsurface negatively layer; the presence of this charged species was proved by its drift under electric field [27]. An other part of the excess of the confined hydrogen at the subsurface layer of the sample is linked to silicon atoms like a dihydride structure (SiH_2). As it was shown by I.R study that the absorption is mainly due to SiH_2 vibration [21, 22].

As we know, silicon is electrochemically unstable in the HF solution due to the presence of the F^- ions, which attack the formed silicon oxide SiO_2 on the surface and allow the passage of current.

In theory, under anodic polarisation n-type silicon is reverse biased and no current should be observed. This behaviour is not well respected and a weak current is observed. This current was ascribed to the injection of electrons into the conduction band by surface states (surface state charge) [9, 10].

In hydrogenated samples this current depends on the duration of treatment in all cases and has saturated value; the observation of a saturated current lets us to think about permanent dissolution of the sample surface following the possible reactions:

$$SiH_2 + 2F^-_{att} \Rightarrow SiF_2 + H_2 + 2e^- \quad \text{(i)}$$

which is an electrochemical reaction where two electrons are injected into the conduction band and

$$H^0 + H^- \rightarrow H_2 + e^- \quad \text{(ii)}$$

which is a chemical reaction and participates by one electron into the conduction band.

If one admits that on the surface the two reactions electrochemically and chemically proceed simultaneously with the four reactions proposed by Memming and Schwandt [3]. Those reactions are as follows:

$$Si + 4OH^-_{ad} + \lambda\oplus \Rightarrow Si(OH)_4 + (4-\lambda)e \quad \lambda\langle 4$$
$$\hookrightarrow SiO_2 + 2H_2O \quad (1)$$

$$SiO_2 + 6HF \Rightarrow H_2SiF_6 + 2H_2O \quad (2)$$

$$Si + 2F^-_{ad} + \lambda\oplus \Rightarrow SiF_2 + (2-\lambda)e \quad \lambda\langle 2 \quad (3)$$

$$SiF_2 + 2\,HF \Rightarrow SiF_4 + H_2$$
$$\xrightarrow{+2HF} H_2SiF_6 \quad (4)$$

OH^-_{ad} and F^-_{ad} are the adsorbed ions, $\oplus$ and e represent holes and electrons respectively. The participation of the hole and electron in the reaction depends on the conduction type of silicon [3]. Reaction (1) and (3) are silicon oxidation and direct silicon dissolution respectively involving charge transfer (electrochemical reactions).

Reaction (2) and (4) are direct dissolution of SiO_2 and SiF_2 by HF, without charge transfer (chemical reaction).

The proposed reaction (i) is the direct electrochemical dissolution of silicon linked (bonded) to two hydrogen in the following manner:

$$SiH_2 + 2F^-_{att} \Rightarrow SiF_2 + H_2 + 2e^-$$
$$\xrightarrow{+4HF} H_2SiF_6 + H_2 \quad \text{(i)}$$

where F^-_{att} is an attracted fluoride ion.

Two electrons are injected in the conduction band and one molecule of hydrogen is generated as gas. Also H_2SiF_6 and H_2 are formed by chemical attack on SiF_2 by HF as in reaction (2) and (4) suggested by Memming and Schwandt [3].

These reactions proceed during the whole anodic polarisation process; thereby the dark currents of hydrogenated samples are greater than those of the non-hydrogenated one. Whereas the observed (OCP) shift of the hydrogenated samples into the negative direction (more negative potentials) compared to the non hydrogenated one, may be explained by the presence of negatively charged layer. This negative charge is due to the presence of H^- on the hydrogenated sample subsurface. This layer slows down the reduction of the H_3O^+ ion to H_2 and evokes the same effect of the hypothesis given by Allongue *et al.* [15], which makes a link between the strong hysteresis and the deposited hydrogen at high rate on the electrode surface.

From the electrochemical point of view the reaction (i) is similar to reactions (3) and (4) if they are applied to one atom of silicon bonded to two atoms of hydrogen rather than to a non bonded one. Reaction (i) proceeds at the same time as the reactions (3) and (4).

One can think that a reaction (5) similar to reaction (1) and (3) will be applied to $=SiH_2$ as follows:

$$=SiH_2 + 4OH^-_{att} \Rightarrow Si(OH)_4 + H_2 + 4e^-$$
$$\hookrightarrow SiO_2 + 2H_2O \quad (5)$$
$$\xrightarrow{+6HF} H_2SiF_6 + H_2$$

But we have favoured reaction (i) rather than reaction (5) in order to rejoin the establishment carried out by Rappich *et al.* [23]. The authors have proved by an IR study the disappearance of SiH_2 binding after its formation, followed by an increase of the transient current under the dark conditions at fixed polarisation of the sample which was immersed in a solution of 0.2M F^- rather than one immersed in 0.1M F^- solution at the same pH (pH = 5). From these results and the increase of the dark current which was directly related to the incorporated quantities of hydrogen as obtained here, one can make a relationship between SiH_2, F^-, the increasing current and the proposed reaction (i).

On n-type silicon Madou e*t al.* [24], by using capacitance measurements, have studied the appearance of an oxide layer on the electrode surface in two solutions at the same pH (pH = 1.7), but the first solution was free of fluoride and the second one was 1M F^-. They have found that the capacitance peak attributed to the oxide appears at (– 0.4 V_{SCE}) in the case of fluoride free solutions and disappears completely at the same potential in the case of a solution of 1M F^- and an other weaker peak appears above (– 0.2 V_{SCE}). This peak reflects the thinness of the oxide layer formed under this condition. These results allow us to say that the existence of F^- ion in solution at lower pH

(pH = 1.7) slows down significantly the oxidation reaction:

$$= SiH_2 + 4OH^-_{att} \Rightarrow Si(OH)_4 + H_2 + 4e^- \rightarrow SiO_2 + 2H_2O \quad (5)$$

to proceed and favour this reaction:

$$= SiH_2 + 2F^-_{att} \Rightarrow SiF_2 + H_2 + 2e^- \xrightarrow{+4HF} H_2SiF_6 + H_2 \quad (i)$$

In this same work the authors kept the concentration of F^- at 1M but they changed the pH value to 8.9 i.e., the concentration of OH^- was increased significantly. They noticed the reappearance of the capacitance peak around –0.6 V_{SCE}, which reflects the reappearance of silicon oxidation at higher pH. They attributed the shift of this capacitance peak towards negative potentials to the increasing of pH value. A similar explanation has been given by Tsuboi *et al.* [25], in which the authors proved that the increasing of pH accelerates porous silicon formation.

Then it seems that the absence of the proposed reactions (i) and (ii), since there is no hydrogen on the silicon surface may explain both the return of the current to the smaller value and the return of (OCP) towards the more positive values for the etched sample and the out-diffused one.

CONCLUSION

The current-potential characteristics of the three durations of time plasma hydrogenation of n-type Si <111> in solutions at a given HF concentration have been investigated; It is found that the anodic dissolution of hydrogenated n-type silicon according to Tafel behaviour occurs at low over potentials; In this potential range, the dissolution involves the same charge transfer coefficient in both sixty minutes and thirty minutes treatment but not the same concentration of the reactants species at the surface samples . The shift of (OCP) and the pore size are related to this difference in the concentration of the reactants species at the surface samples.

At over potentials a permanent dissolution of SiH_2, according to the proposed reaction (i) inject two electrons into the conduction band and causes the increase of the dark current at anodic polarisation.

The participation of the reaction (i) may explain the mass-loss, and the pore sizes observed by SEM, in the case of hydrogenated samples.

The negative shift in V_{fb}(H) is not well discussed in this present paper. Research investigations in this direction are currently in progress in which we try to establish a describing model of the properties of Hydrogenated layer and the negative shift in V_{fb}(H). Working under fluoride basic solutions will take our intention in order to agree the elimination of the reaction (5).

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