METHOD OF ETCHING A SILICON-BASED MATERIAL

Field of Invention

The invention relates to a method of etching a silicon-based material.

Background Art

Selective etching of silicon-based materials to create silicon pillars is known to be of benefit, for example, in creating anodes for lithium-rechargeable batteries. One such approach is described in US-7033936, which is incorporated herein by reference. According to this document, pillars are fabricated by creating a mask by depositing hemispherical islands of caesium chloride on a silicon substrate surface, covering the substrate surface, including the islands, with a film, and removing the hemispherical structures (including the film covering them) from the surface to form a mask with exposed areas where the hemispheres had been. The substrate is then etched in the exposed areas using reactive ion etching and the resist is removed, e.g. by physical sputtering, to leave an array of silicon pillars in the unetched regions, i.e. in the regions between the locations of the hemispheres.

An alternative, chemical approach is described in Peng K-Q, Yan, Y-J, Gao S-P, and Zhu J., Adv. Materials, **14** (2002), 1164-1167, Adv. Functional Materials, (2003), 13, No 2 February, 127-132 and Adv. Materials, **16** (2004), 73-76 . Peng, *et al.* have shown a way to make nano pillars on silicon by a chemical method. According to this method, a silicon wafer, which may be n- or p-type and has the {111} face exposed to solution, is etched at 50^{o}C using the following solution: 5M HF and 20mM $AgNO_3$. Pillars are formed at about 20 microns/hr and pillar heights up to 24 microns are reported. Apart from height, no other dimensional data is given, such as mean pillar diameter, packing density, or surface uniformity. The method is only carried on chips of

about $1cm^2$. The mechanism postulated in these papers is that isolated nanoclusters of silver are electrolessly deposited on the silicon surface in an initial stage. In a second stage, the silver nanoclusters and the areas of silicon surrounding them act as local electrodes that cause the electrolytic oxidation of the silicon in the areas surrounding the silver nanoclusters to form SiF_6 cations, which diffuse away from the etching site to leave the silicon underlying the silver nanocluster in the form pillars. It is suggested that metals other than silver, e.g. Ni, Fe, Co, Cr and Mg, especially in the form of nitrate salts, could be used to form silicon pillars.

K. Peng *et al.*, Angew. Chem. Int. Ed., **44** (2005), 2737-2742; and K. Peng *et al.*, Adv. Funct. Mater., **16** (2006), 387-394, relate to an etching method that is similar to that described in the earlier papers by *Peng et al* but the nucleation/ silver nanoparticle deposition step and the etching step are performed in different solutions. In a first (nucleation) step, a silicon chip is placed in a solution of 4.6M HF and 0.01M $AgNO_3$ for 1 minute. A second (etching) step is then performed in a different solution, namely 4.6M HF and 0.135M $Fe(NO_3)_3$ for 30 or 50 minutes. Both steps are carried out at 50^oC. Pillars of about 6 and 4 microns in height, and about 20 and 20 to 40 nm in diameter, respectively, are reported. Pillars are grown in the {111} direction on the {111} plane. Neither the pillar packing density (surface uniformity), nor the size of silicon chip used are disclosed. The silicon wafer may be n- or p-type. In these papers, a different mechanism is proposed for the etching step as compared to the earlier papers, namely that silicon underlying the silver (Ag) nanoparticles are removed and the nanoparticles gradually sink into the bulk silicon, leaving columns of silicon in the areas that are not directly underlying the silver nanoparticles.

There is a need for higher pillars, increased density of pillars and improved uniformity of pillar distribution. In addition, it would be desirable to increase the speed of pillar formation (etching). Furthermore, because the approaches described in *Peng* are restricted to the {111} face, the applicability of these approaches is limited.

Disclosure of the Invention

The invention is set out in the claims.

A method is now described according to which an improved chemical method is provided for creating silicon pillars on a silicon-based substrate.

Starting with chips (which may be about 1 to 15 cm^2) taken from a silicon wafer, in standard semiconductor material, one side of the chip is polished, while the other side is distressed (roughened). The plane of the wafer corresponds to the {100} or {110} crystal plane of silicon. The silicon may be doped, e.g. using any conventional doping agent, to make the silicon n-type or p-type as desired. The typical resistivity of the silicon chip is 1 ohm cm plus or minus two powers of ten. For example in the case of n-type silicon, the resistivity is typically and approximately one ohm cm and it will be noted that the doping level is not critical in the embodiments described herein.

Before being subjected to the method of the present invention, the surface may be rendered uniformly clean and hydrophilic using an RCA-1 etch (namely water: 88 ammonia: concentrated hydrogen peroxide, in the volume ratio of 1:1:1). In the next preparation stage, the silicon chip can be protected on its back (rougher) side by a thin Au/Cr coating (e.g. 10Au/1Cr, ca 200 nm thick film).

The etching method comprises two stages. The first stage is nucleation in which discrete metal deposits are formed on the silicon surface and the second stage is the actual etching of the substrate. The carrying out of these two stages in accordance with the present invention results in a more uniform pillar array in terms of both density and height.

The first nucleation stage forms discrete metallic deposits on the surface of the silicon. The chemical composition of the aqueous solution used in the nucleation stage in one embodiment is:

- 1 to 40% v/v of an alcohol, e.g. ethanol; typical alcohol contents of the solution are 5 to 40%, e.g. 15 to 40%, optionally about 5 or 6 % v/v, based on the total volume of the whole aqueous solution;
- 1.5 to 10 molar (M) hydrofluoric acid, e.g. 5 to 7.5M, for example about 6.8M (Examples of typical concentrations are 4.5- 9M, e.g. 6.8 to 7.9M; it should be noted that 4.5M, 6.8M, 7.9Mand 9M solutions of HF or a fluoride salt correspond, respectively, to the inclusion within the solutions of 20%, 30%, 35% and 40% by volume of concentrated (40%) HF);
- 5 to 100mM, e.g. 10 to 65mM of a metal salt that will electrolessly deposit in discrete areas on the silicon substrate in the presence of fluoride ions, the salt optionally being a silver salt, e.g. silver nitrate; the concentration of the salt may be 12.6 to 24 mM, e.g. 24mM. (It should be noted that a12.6 to 22.1mM solution is the equivalent of a solution containing 40 to 70% of a 31.5mM silver solution and a 24mM solution is the equivalent of a solution containing 40% of a 0.06M (60mM) silver solution).

The temperature at which the nucleation reaction is carried out at may be 0 to 30°C and, for example room temperature (20°C). The nucleation reaction will

occur rapidly, e.g. within 10 seconds, but the substrate may be in contact with the substrate for up to about 15 minutes, e.g. about 10 minutes. The inclusion of an alcohol, e.g. ethanol and the act of carrying out the nucleation stage at a relatively low temperature, e.g. at room temperature, has the effect of slowing down the chemical processes. Hence a more even distribution of the metal deposits, e.g. silver, is achieved and more evenly spaced pillars are subsequently obtained.

The second stage is etching, during which the silicon pillars are formed. The solution used in the etching stage may be the same or different to that used in the nucleation stage. If the same solution is used, the second (etching) stage may follow on seamlessly from the first (nucleation) stage and the overall duration of the first and second stages is generally in the region of 5 to 50 minutes. If a different solution is used, the first nucleation stage may generally be 5 to 10 minutes. The solution used in the etching stage may be:

- hydrofluoric acid (HF); the concentration of fluoride ions may be 4 to 15 M e.g. 4.5 to 8M;
- a metal salt that can oxidise silicon in the presence of fluoride ions; the salt is optionally a silver salt or a ferric salt; and preferably silver or ferric nitrate salt. The concentration of the salt may be 10 to 40 mM e.g. 20 to 30 mM, for example about 25mM.

Alcohol is not necessary in the etching stage.

The etching stage is optionally, depending upon doping density, carried out at a temperature higher than that of the nucleation stage; the temperature increase between the two stages may be at least 20°C, e.g. at least 35°C; the etching stage may be performed at a temperature of 30 to 80°C, e.g. 45 to 75ºC, such as 60° to 75°C; within about 45 minutes, pillars of consistent height of about 70 to

75 microns in height and 0.2 microns in diameter can be achieved. The etching stage may be conducted for a shorter period of time but the columns will be shorter.

The resulting silicon-based substrate with its attached silicon pillars may be used as the anode for a lithium-ion rechargeable battery since the inventor believes that the silicon pillars can reversibly react with lithium ions without being broken up or destroyed, thus providing good capacity retention over a large number of charge/discharge cycles. Alternatively the pillars may be sheared from the part of the substrate that has not been etched to form silicon fibres. The substrate of the present invention finds particular application in the electrodes of lithium-ion cells.

The pillar surface density (fractional coverage) may be described by the following ratio F:

$$F = P/[R+P]$$

wherein P is the amount of silicon present as pillars, and R is the amount of silicon removed.

For a fixed pillar height, the larger the value of F, the greater the reversible lithium ion capacity per unit area and so the greater the electrical capacity of an electrode. Also the greater the value of F, the larger the amount of silicon material that may be harvested to create silicon fibre. The pillar packing density F is maximised by the nucleation stage and the applicants have achieved fractional coverages of up to 40%.

In the process described above, F is typically about 15 to 20%.

In one embodiment, the invention provides a method of etching a silicon substrate comprising contacting the silicon substrate with a solution of an etching fluoride acid or fluoride salt, a silver salt and an alcohol. The silver salt is water soluble, e.g. silver nitrate. The silver nitrate content of the solution may be in the range 40 to 70%, based on a 31.5 mM solution of silver nitrate, which is equivalent to a silver nitrate concentration in the final solution of 12.6 to 22.1 mM silver nitrate. The fluoride acid may comprise hydrogen fluoride whose content in the solution is between 30% and 40% by volume, based on concentrated (40% or 22.6 M) HF, which is equivalent to an HF concentration in the final solution of 6.8 to 9 M), e.g. in the range 35 to 40% (HF concentration in the final solution of 7.9 to 9 M), for example 40% (HF concentration in the final solution of 9 M). The alcohol may be ethanol, the content of which in the final solution may be in the range of 15 to 40%. The solution may also include water in the range of 10 to 30%, e.g. 20%.

The method may include the stage of allowing the substrate to stand in solution at a temperature in the range of 10 to 30°, e.g. 20°C, for a period in the region of 5 to 50 minutes, e.g. 10 minutes. The method may further include raising the temperature of the solution to a temperature in the range of 20 to 75°C for a period of 40 to 45 minutes, e.g. 45 minutes.

The method may include subsequently adding further silver or silver nitrate, e.g. 5 to 10% further silver or silver nitrate, such as 6%. When the temperature is raised, as mentioned in the preceding paragraph, further silver may be added upon raising the temperature and the two further amounts may be added at each of 10 and 20 minutes subsequently.

The etching may be performed on the {100} or {110} plane.

The invention also provides an etched silicon substrate made by a method as described above.

The following two examples illustrate the claimed process:

Example 1

A clean silicon sample (ca. 1cm^2, 2 - 5 ohm cm n-type material that has been back coated as described above) is placed, face up ({100} face), in a polypropylene beaker with 50ml of an etching solution. The composition of the etching solution was:-

12.5ml HF (40%);

2.5ml ethyl alcohol;

35ml of 31.5mM $AgNO_3$.

which corresponds to an aqueous solution containing:

5.7M of HF;

5% v/v ethyl alcohol;

22mM of $AgNO_3$.

The sample is left at room temperature (ca. 20^{o}C) for 10 minutes in order to obtain uniform nucleation of silver on the sample face. As discussed below, the ethanol (or other alcohol) is essential in its modification to the HF chemistry.

The etching stage follows on from the nucleation stage. In the etching stage, the silicon substrate submerged in the above solution is placed in a constant temperature bath at e.g. 75^{o}C for 45 minutes; in other words the solution used in the etching stage is the same as the solution used in the nucleation stage. Depending on precise conditions and especially the duration of the method, this treatment etches the silicon and results in pillars of 20 to 100 microns in height, typically 60 to 100 microns, in height.

Example 2

According to an alternative approach, starting with a master solution that consists of:

- 20ml 0.06M $AgNO_3$ (24mM in the final solution);
- 17.5ml conc. HF (7.0M in the final solution);
- 2.5 ml EtOH (5%v/v in the final solution); and
- 10 ml H_2O

(50ml total). One of the following procedures (a) to (c) is then carried out:

(a) A clean silicon sample (ca. $1cm^2$, 2 - 5 ohm cm n-type material that has been back coated as described above) is placed, face up ({100} face), in a polypropylene beaker with 50ml of the above master solution at 20^oC for 10 minutes. Directly following on from this, the temperature is raised to 53^oC and at the same time further silver salt is added, in this case by adding 3ml of 0.6M $AgNO_3$ solution is added. After 45 mins, the chip is removed and rinsed. The resulting pillars are ~85 microns high, which is 50% greater than obtained without the second addition of 3ml of 0.6M $AgNO_3$ solution.

(b) A clean silicon sample (ca. $1cm^2$, 2 – 5 ohm cm n-type material that has been back coated as described above) is placed, face up ({100} face), in a polypropylene beaker with 50ml of the above master solution at 20^oC for 10 minutes. Directly following on from this stage, the temperature is raised to 53^oC for the etching stage and at the same time 1ml of 0.6M $AgNO_3$ solution is added. After 10 minutes a further 1ml of 0.6M $AgNO_3$ solution is added, and after a further 10 minutes another 1ml of 0.6M $AgNO_3$ solution is added. The total time at 53^oC is 45 minutes, resulting in uniform pillars 85 to 100 microns high and 0.2 microns in average diameter.

Such further additions of silver nitrate solution may be made during the course of the etching stage, for example, at the 15^{th}, 25^{th} and 35^{th} minute of the reaction or, for example, at the 10^{th} and 20^{th} minute of the reaction. In this process, the fractional coverage, F, is calculated to be 15 to 20%.

(c) A clean silicon sample (ca. $1cm^2$, 10 ohm cm n-type material that has been back coated as described above) is placed, face up ({100} face), in a polypropylene beaker with 50ml of the above master solution at 20^oC for 10 minutes and then transferred to a new solution for the etching stage, which may, for example, be composed as follows:

20ml water;

12.5 ml 60mM $Fe(NO_3)_3$ (aq); and

17.5ml 40% HF.

Uniform pillars of 40 microns in height are achieved in 45 minutes. F is measured using SEM analysis and is approximately 30%. Variation in the concentration of $Fe(NO_3)_3$ results in a variation in pillar diameter between about 0.2 to 0.6 microns.

Continuous or step-wise addition of $Fe(NO_3)_3$ and / or $AgNO_3$ solution during the etching process gives both improved uniformity and increased pillar height.

It is found that the approach of the present invention provides an increasing pillar height of approximately five times that previously obtained and significantly improved pillar uniformity over several square centimetres. As a result, silicon based electrodes can be fabricated with uniform height and packing density across wafers of 10 to 15 centimetres in diameter. Alternatively the pillars can be grown for subsequent detachment or "harvesting" for example for creating a battery anode as described in more

detail in the co-pending UK patent application 0601319.7 entitled "A method of fabricating fibres composed of silicon or a silicon-based material and their use in lithium rechargeable batteries.", co-assigned herewith and incorporated herein by reference.

It has been found that the inclusion of an alcohol, for example a C_{1-4} alkanol, such as ethanol, in the nucleation step provides a number of advantages.

Firstly, in terms of nucleation effects, the ethanol addition gives a more uniform silver deposition in the first, vital, period (ca. 10 seconds duration). This leads to a more uniform spatial distribution of pillars.

The effects of ethanol addition can be further understood when considering the composition effects. In particular, varying the ethanol concentration (by changing the water/alcohol ratio but maintaining the total volume at 50 ml) has an important effect on pillar height, which is believed to occur at the nucleation stage. Thus if the concentration is increased beyond 5% v/v (i.e. 2.5 ml of ethanol in the 50 mil total solution amount), the tendency is to decrease the pillar height. Further data is set out in the table below:

Effect of ethanol (EtOH) concentration on pillar height

Vol. EtOH (ml) in 50 ml total solution volume	Nucleation Time (min)/temp^{o}C	Pillar growth Time (min)/temp^{o}C	Pillar height Microns*
5 (10%)	10/20	45/20	20
5 (10%)	10/20	45/45	35
5 (10%)	10/20	45/70	40
10 (20%)	10/20	45/20	13
10 (20%)	10/20	45/45	22
10 (20%)	10/20	45/70	20

20 (40%)	10/20	45/20	10
20 (40%)	10/20	45/45	~0
20 (40%)	10/20	45/70	~0

In terms of temperature effects, nucleation occurs very quickly, <10 seconds. The room temperature nucleated pillars are taller than those obtained at higher nucleation temperatures and thus the inventor believes there is greater control of the process when using room temperature for the nucleation stage. If for a 10 ohm cm n-type silicon wafer, the temperature is held at room temperature (20° to 25°C) for 10 minutes for nucleation, and then raised to 50°C for 45 minutes for the etching stage, then the pillar height will be ~30 microns. Between 70°C and 75°C, the pillar height will be ~60 microns.

Pillars in the range of ~75 microns in height can be obtained in 45 minutes. Pillars up to 120 microns in height have also been obtained. One reason for the increased height observed by using this method is the inclusion of a small amount of $AgNO_3$ (1ml, 60 mM added in 50ml solution) in the $Fe(NO_3)_3$ etching solution.

If the etching stage is carried out at 80°C for the same time, the pillars, although forming initially, are destroyed. However, if the etching time is reduced for an etching stage conducted at 80°C, then pillars are apparent. This last result may arises because there is some lateral etching that results in a tapered pillar structure and the ratio of the lateral to vertical etching rate increases with temperature. However, the precipitate collapse in pillar formation at 80°C is more likely to be explained by the loss of protective adsorbates on the {110} plane.

It is found that the level of doping in the resistance in the range 0.1 ohm cm to 1,000 ohm cm has no effect. Also the process works for both n- and p-type silicon. In the 1 to 10 ohm cm range, p-type silicon has been found to etch slightly faster than n-type silicon. Furthermore, pillar growth is not limited to {100} plane. Growth of silicon structures are also observed on the {110} plane including pillars and sheets inclined at an angle of approximately 45° to the surface plane.

Etching on the {100} plane will give pillars that are at a right angle to the wafer plane. On the {110} plane, pillars at a 45° angle to the wafer plane are produced. Furthermore vertical pillars can be grown on the {111}, with protective adsorbates on the (110) faces. The etch rates are in the order {100} >{111} >> {110}.

Harvesting of silicon fibres is generally carried out using ultrasonics, because harvesting using a knife gives a large amount of particulate silicon in addition to the fibre material.

The etching process can also be carried out either on very large scale integration (VLSI) electronic grade single crystal wafers or rejected samples of the same. As a cheaper alternative, photovoltaic grade polycrystalline material may also be used. An even cheaper material that may be used is crystalline metallical grade silicon.

It will be appreciated that the pillar structure created by the methods described above can be used in any appropriate implementation including silicon anodes for use in rechargeable lithium-ion cells. Although the structures described herein are termed “pillars” it will be recognised that any appropriate pillar-like, fibre-like or hair-like structure is embraced. It will further be recognised that

the parameters set out above can be varied as appropriate and that the material can extend beyond pure-silicon based material with appropriate doping to, for example, a silicon germanium mixture.

Reference herein to silicon-based material include pure silicon or doped silicon or other silicon-based material such as a silicon-germanium mixture or any other appropriate mixture. The substrate from which pillars are created may be n- or p- type, ranging from 100 to 0.001 Ohm cm, or it may be a suitable alloy of silicon, for example Si_xGe_{1-x}.

Other alcohols may be used in place of ethanol and other etching agents such as fluoride salt such as ammonium fluoride may be used. .

Etching and nucleation are both galvanic exchange reactions, e.g.

$$Si + 6F^- + 4Ag^+ = (SiF_6)^{2-} + 4Ag$$

Other soluble silver salts may be used in the place of silver nitrate and alternative metals with soluble salts especially nitrates providing a galvanic exchange reaction may be adopted, for example a metal that is near to or less electro-positive than silver. Nucleation requires metal salts, while etching can use either metal ions or non-metallic ions such as hydrogen ions or nitrate ions (or both) provided that their reduction potential is in, or near to, the range 0 to 0.8V, on the normal hydrogen scale. The articles by *Peng et al* mentioned above mention alternative metals that may be used in place of silver. Metal ions that have a potential between +0.8V and 0.0V (vs standard hydrogen electrode (SHE)), such as Cu^{2+} ions (at +0.34V (vs SHE)) may be used instead of the silver ions).

Claims

1. A method of etching a silicon substrate until pillars are formed comprising contacting the silicon substrate with an aqueous solution of:
   - a fluoride acid or a fluoride salt, whose content is 1.5-10M;
   - metal salt, whose content is 5-100mM, capable of electroless deposition of the metal on the silicon in the presence of fluoride ions, and
   - an alcohol, whose content is in the range of 1-40% by volume.

2. A method as claimed in claim 1 in which the metal salt is a silver salt, optionally silver nitrate.

3. A method as claimed in claim 2 in which the silver nitrate content of the solution is in the range of 0.2 to 16%, e.g. 0.75% to 0.7% by weight.

4. A method as claimed in claim 1 or claim 2 in which the metal salt content, e.g. the silver or silver nitrate content, of the solution is in the range of 5 to 100mM, and in the range 12.6 to 24mM.

5. A method as claimed in any preceding claim in which the fluoride acid comprises hydrogen fluoride whose content is between 3 and 20% by weight, e.g. between 8 and 20%, for example between 10 and 15%, such as about 12 or 13.6%.

6. A method as claimed in any preceding claim in which the etching fluoride acid comprises hydrogen fluoride whose content is between 1.5 and 10M, e.g. between 5 and 7.5M, for example about 6.8M.

7. A method as claimed in any preceding claim in which the alcohol is ethanol.

8. A method as claimed in any preceding claim in which the alcohol content is in the range of up to 40% by volume, and in the range 3% to 40%, e.g. 5 to 40%, such as 15 to 30%.

9. A method as claimed in any preceding claim further comprising the stage of allowing the substrate to stand in solution at a temperature in the range 0ºC to 30°C, e.g. 20°C.

10. A method as claimed in claim 9, wherein said standing step lasts for a period in the region of 5 to 50 minutes, e.g. about 10 minutes.

11. A method as claimed in any preceding claim further comprising raising the temperature of the solution to a temperature in the range 40ºC to 75°C.

12. A method as claimed in claim 11, wherein the substrate is allowed to stand in the solution at the raised temperature for a period in the region of 30 to 100 minutes, for example about 45 minutes.

13. A method as claimed in any preceding claim further comprising adding further silver salt, e.g. silver nitrate, or a ferric salt, e.g. ferric nitrate, during the course of the method.

14. A method as claimed in claim 13 wherein the amount of the silver salt or ferric salt added is in the range of 0.1 to 2% by weight, e.g. about 1% by weight.

15. A method as claimed in claim 13 or 14 wherein the further silver salt or ferric salt is added in an amount that increases the silver or ferric concentration of the solution by 2 mM to 6 mM, e.g. 2.85 mM to 5.45mM.

16. A method as claimed in any of claims 13 to 15, when dependent on claim 11 or 12, in which the further silver salt or the ferric salt is added upon raising the temperature.

17. A method as claimed in claim 16 in which a first amount of a silver salt or ferric salt is added upon raising the temperature and then at least one further amount is added, e.g. at 10 and 20 minutes subsequently.

18. A method of etching a silicon substrate as claimed in any of claims 1 to 11 wherein the said contacting step forms a first stage using a first solution and the method further comprises:
a second stage comprising contacting the silicon substrate with a second solution comprising a fluoride acid and a ferric salt, e.g. $Fe(NO_3)_3$.

19. A method as claimed in claim 18, wherein the substrate is allowed to stand in the first solution for a period in the region of up 15 minutes, e.g. about 10 minutes.

20. A method as claimed in claim 18 or 19 wherein the second stage is conducted at a temperature above that of the first stage, e.g. a temperature in the range of 30 to 80°C, for example 45 to 75ºC, such as 60° to 75°C.

21. A method as claimed in any of claims 18 to 20 wherein the second stage is conducted for a period in the region of 40 to 50 minutes, for example about 45 minutes.

22. A method as claimed in any of claims 18 to 21 wherein the second solution includes a silver salt, e.g. in an amount up to 60mM.

23. A method as claimed in any of claims 18 to 22, further comprising adding a silver salt or a ferric salt, e.g. $Fe(NO_3)_3$ and/or $AgNO_3$, to the solution during the course of the method, especially to the second solution during the second stage.

24. A method as claimed in claim 23, wherein the amount of further silver or ferric salt that is added is an amount that increases the silver or ferric concentration of the solution by up to 10mM, e.g. 2 to 6mM.

25. A method as claimed in claim 23 or claim 24 in which the silver or ferric salt is added to the second solution in two or more occasions.

26. A method as claimed in any of claims 18 to 25 wherein the substrate is allowed to stand in the second solution for a period in the region of 40 to 50 minutes, e.g. 45 minutes.

27. A method as claimed in any preceding claim in which etching is performed on the {100} plane or the {110} plane or the {111} plane.

28. An etched silicon substrate created by a method as claimed in any preceding claim.

29. A lithium rechargeable cell comprising an anode that comprises an etched silicon substrate as claimed in claim 28.