

(19)



**Octrooi Centrum
Nederland**

(11)

2014588

(12) B1 OCTROOI

(21)

Aanvraagnummer: **2014588**

(22)

Aanvraag ingediend: **07/04/2015**

(51)

Int. Cl.:

H01M 4/134 (2010.01) **H01M 4/04** (2016.01) **H01M 4/1395** (2016.01) **H01M 4/36** (2016.01) **H01M 4/38** (2016.01) **H01M 10/0525** (2016.01)

(43)

Aanvraag gepubliceerd:
11/01/2017

(47)

Octrooi verleend:
19/01/2017

(45)

Octrooischrift uitgegeven:
16/03/2017

(73)

Octrooihouder(s):

**Stichting Energieonderzoek Centrum
Nederland te Petten.**

(72)

Uitvinder(s):

Wilhelmus Jozef Soppe te Petten.

(74)

Gemachtigde:

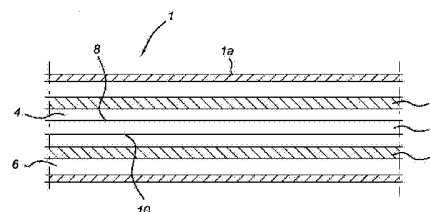
ir. M.F.J.M. Ketelaars c.s. te Den Haag.

(54)

Rechargeable battery and method for manufacturing the same.

(57)

Rechargeable battery comprising at least an electrolyte layer (2), a cathode layer (4) and an anode layer (6); the electrolyte layer (2) comprising a lithium salt compound arranged between a cathode surface (8) of the cathode layer (4) and an anode surface (10) of the anode layer (6). The anode layer (6) is a nanostructured silicon thin film layer comprising a plurality of silicon columns (12), wherein the silicon columns (12) are directed in a first direction perpendicular or substantially perpendicular to the anode surface (10) of the silicon thin film layer. The silicon columns are arranged adjacent to each other while separated by grain-like column boundaries (14) running along the first direction. The silicon columns (12) comprise amorphous silicon.



Rechargeable battery and method for manufacturing the same

Field of the invention

The present invention relates to a rechargeable battery, in particular a lithium-ion rechargeable battery provided with silicon-based anode material. In a further aspect the present invention relates to a method of manufacturing a rechargeable battery.

Prior art

Current state of the art lithium-ion batteries typically employ graphite as anode material, wherein storage capacity of graphite is around 370 mAh/g. It is known that silicon anode material has a much larger theoretical capacity of around 4200 mAh/g, but the intercalation process of lithium leads to a volume increase of the silicon anode material as high as 300% or even more. One of the main problems with bulk silicon anode material is that it pulverizes quickly during the intercalation process and that it loses its functionality after a relatively small number of charging cycles.

In order to deal with the volume expansion of silicon anode material and to reduce cracking and pulverization thereof during charging cycles, several silicon anode solutions have been proposed, such as silicon nanowires, nanotubes, porous silicon or to mix silicon with graphite, see for example Ning Ding, Journal of Power Sources 192 (2009) 644–651, “Improvement of cyclability of Si as anode for Li-ion batteries” and Uday Kasavajjula, Journal of Power Sources 163(2007) 1003-1039, “Nano- and bulk-silicon-based insertion anodes”.

Many of the proposed solutions to manufacture silicon anode material are unattractive as various complex manufacturing steps are required, making the manufacturing process rather expensive. Also, many of the proposed solutions are not readily scalable to high yield industrial production levels for commercialization.

Summary of the invention

The present invention seeks to provide an rechargeable battery, in particular a lithium ion battery comprising silicon anode material having an improved storage capacity per unit weight and reduced capacity fading.

According to the present invention, a rechargeable battery of the type defined in the preamble is provided comprising at least an electrolyte layer, a cathode layer and an

anode layer. The electrolyte layer comprises a lithium salt compound and is arranged between a cathode surface of the cathode layer and an anode surface of the anode layer. The anode layer is a continuous nanostructured thin film layer comprising a plurality of adjacent columns, the columns extending in a perpendicular direction from the anode surface. The plurality of columns are arranged “continuous”, i.e., adjacent to each other while separated by interfaces extending in the perpendicular direction. The plurality of columns comprise silicon and have an amorphous structure.

The advantage of the rechargeable battery according to the present invention is that lithium ion (de)intercalation in or out of the anode layer, i.e. the nanostructured thin film layer, is greatly facilitated by the plurality of columns and the interfaces between them. The plurality of columns and interfaces provide improved lithium ion accessibility in and out of the amorphous structure of the columns that comprise silicon in the anode layer during lithium ion insertion and extraction, so that the storage capacity per unit weight of the anode layer is significantly increased and capacity fading over multiple recharging cycles is reduced.

According to an aspect of the invention, the amorphous structure comprises up to about 30% of a nano-crystalline structure. According to an embodiment, the anode layer thus consists of an amorphous columnar material as defined above, in which nano-crystalline regions exist.

The anode layer comprises a silicon-based material.

According to an aspect of the invention, the material of the columns comprises amorphous silicon.

According to an aspect of the invention, the material of the columns comprises a silicon alloy or silicon based mixture. According to an embodiment, the silicon alloy or silicon based mixture has an amorphous structure.

The silicon alloy may be either an addition or an alternative to the amorphous silicon. Thus, according to an aspect of the invention, the material of the columns comprises at least one material selected from amorphous silicon and amorphous silicon alloy.

According to a further aspect, the material of the columns comprises amorphous silicon and nano-crystalline silicon alloy.

In some embodiments, the silicon alloy may be present in the anode layer as a nano-crystalline phase.

According to an embodiment, the silicon alloy or silicon based mixture is selected from a group of alloys or mixtures comprising Si-C, Si-N, Si-Ge, Si-Ag, Si-Sn.

In a further aspect, the present invention relates to a method for manufacturing a rechargeable battery comprising at least an electrolyte layer, a cathode layer and an anode layer. The method comprises the steps of

forming on a substrate a continuous nanostructured thin film layer as an anode layer, wherein the forming process is configured to create the continuous nanostructured thin film layer comprising a plurality of adjacent columns, the columns extending in a perpendicular direction from the substrate and arranged adjacent to each other while separated by interfaces extending in the perpendicular direction.

The columns comprise silicon and have an amorphous structure.

The method further comprises

providing a lithium salt compound as the electrolyte layer and

arranging the electrolyte layer between a cathode surface of the cathode layer and an anode surface of the anode layer.

The advantage of the method of the present invention is that the forming process is a self-organizing and spontaneous process for forming on a substrate a continuous amorphous layer nanostructured with a plurality of columns and interfaces there between, yielding a rechargeable battery having an increased storage capacity per unit weight and a reduced capacity fading.

According to the method, the interfaces in the nanostructured amorphous anode layer will locally be perpendicular to the surface with the electrolyte layer.

In some embodiments the method stimulates dendritic or multibranch growth of silicon columns, wherein the grain-like or crystal-like engagement between adjoining silicon columns is maintained.

The method of the present invention is essentially a single step manufacturing process without the need for pre- or post-treatment method steps for e.g. the substrate and/or the silicon anode layer, thereby facilitating industrial production levels for commercialization.

Short description of drawings

The present invention will be discussed in more detail hereinafter based on a number of exemplary embodiments with reference to the drawings, in which

Figure 1 shows a cross section of an embodiment of a rechargeable battery according to the present invention;

Figure 2 shows a screen image from an electron microscope depicting a cross section of an embodiment of a nanostructured silicon thin film layer according to the present invention; and

Figure 3 shows a screen image from an electron microscope depicting a top view of an embodiment of a nanostructured silicon thin film layer according to the present invention.

10 Detailed description of exemplary embodiments

Figure 1 shows a cross section of an embodiment of a rechargeable battery 1 according to the present invention. In the embodiment shown, the rechargeable battery 1 comprises at least an electrolyte layer 2, a cathode layer 4 and an anode layer 6, wherein said layers 2, 4, 6 are enclosed by a housing 1a. The electrolyte layer 2
15 comprises a lithium salt compound that is arranged between a cathode surface 8 of the cathode layer 4 and an anode surface 10 of the anode layer 6. The cathode layer 4 as well as the anode layer 6 are each arranged on a respective substrate 5.

In Figure 2 an exemplary embodiment of an anode layer according to the invention is shown. The anode layer 6 comprises a nanostructured silicon thin film
20 layer comprising a plurality of silicon columns 12 or columns 12 arranged on the substrate 5. The nanostructured silicon thin film layer has a measured crystal fraction of zero or substantially zero, so the nanostructured silicon thin film layer comprises amorphous silicon (a-Si), in particular the plurality of silicon columns 12 or columns 12 comprise amorphous silicon.

In light of the present invention the term “amorphous silicon” should be construed as comprising protocrystalline silicon, which is a definition for amorphous silicon comprising a small fraction of nano-crystalline silicon. This small fraction may be up to about 30% of the nanostructured silicon thin film layer. So for ease of reference the term amorphous silicon will be used hereinafter to indicate that the largest
30 fraction of the nanostructured silicon thin film layer comprises amorphous silicon, in which the nanostructured silicon thin film layer may or may not comprise a relatively small fraction of nano-crystalline silicon.

Furthermore, it is noted that additionally or alternatively to “silicon”, the columns may comprise a silicon-based material, i.e., a silicon based alloy or silicon based mixture. Thus the term “silicon” should also be construed as comprising silicon-based materials, i.e., silicon based alloys or silicon based mixtures.

5 According to an embodiment, the amorphous silicon comprises n-type or p-type dopants to obtain a nanostructured silicon thin film layer of either n-type conductivity or p-type conductivity, respectively.

 According to an embodiment, the silicon alloy is selected from a group of silicon based alloys or silicon based mixtures comprising Si-C, Si-N, Si-Ge, Si-Ag and
10 Si-Sn.

 According to the invention, the columns may comprise either amorphous silicon or amorphous silicon alloy or a combination of amorphous silicon and amorphous silicon alloy.

 Also, the anode layer may comprise a mixture of an amorphous material and
15 nano-crystalline phase. For example, a mixture of amorphous silicon and nano-crystalline silicon, or a mixture of amorphous silicon with nano-crystalline silicon alloy, or an mixture of silicon and silicon based alloy predominantly in an amorphous state comprising a small fraction (less than about 30%) of the mixture in a nano-crystalline state.

20 According to the present invention, the amorphous silicon columns 12 are extending in a perpendicular direction from the anode surface 10, i.e., the interface between the anode layer and the electrolyte layer, in which the plurality of silicon columns 12 are arranged adjacent to each other while separated by interfaces extending perpendicularly to the anode surface 10.

25 The rechargeable battery 1 of the present invention exhibits a higher storage capacity per unit weight than prior art lithium ion batteries as the plurality of silicon columns 12 and interfaces 14 there between improve the accessibility and diffusion of lithium ions in and out of the nanostructured silicon thin film layer during a charging cycle, i.e. during lithium (de)intercalation. As a result, specific storage capacity of up to
30 4000 mAh/g is achievable with the rechargeable battery 1 of the present invention.

 In an embodiment, the interfaces 14 resemble grain-like column boundaries 14 between the columns that extend in the perpendicular direction. According to the invention, the term “grain-like column boundaries” refers to a type of interface or

region between adjoining silicon columns 12 (domains) that resemble grain or crystal boundaries as customarily defined for grains consisting of crystalline atomic lattices. So, although the plurality of silicon columns 12 comprise amorphous silicon-based material, the silicon columns 12 exhibit a grain-like engagement between adjoining
5 columns.

It is the interface 14 boundary between adjoining silicon columns 12 that provides the rechargeable battery 1 of the present invention with improved storage capacity per unit weight as well as improved lithium diffusion between the silicon columns 12 due to sufficient porosity of the interfaces in the nanostructured silicon thin
10 film layer.

In some embodiments the nanostructured silicon thin film layer comprises at least in part free space between the plurality of silicon columns 12 in addition to the columnar interfaces engagement there between, in which the free space further facilitates volumetric changes during charging and discharging cycles of the
15 rechargeable battery 1, hence reducing capacity fading.

In a further embodiment, the silicon columns 12 also comprise dendritic or multibranch silicon columns 12, thus having the silicon columns 12 comprising tree-like branches of amorphous silicon.

In these embodiments the above mentioned grain-like or crystal-like
20 engagement between adjoining silicon columns 12 remains present at particular contact regions, points or lines between said columns 12.

To further explain the complex and novel structure of the nanostructured silicon thin layer of the present invention, Figure 3 shows a top view of an embodiment of the nanostructured silicon thin film layer. In the embodiment shown, the plurality of silicon
25 columns 12 are depicted as brighter areas or granular spots and form a grain-like or “poly crystalline” pattern. The column boundaries 14 between the plurality of silicon columns 12 are depicted as darker areas separating the granular spots. From Figure 3 it is further seen that the grain or granular pattern resembles a poly-crystalline structure even though the plurality of silicon columns 12 are proto-crystalline i.e., comprise
30 amorphous silicon and possibly a small fraction of nano-crystalline silicon. This complex and unique granular pattern between the plurality of silicon columns 12 provides the nanostructured silicon thin film layer with its improved storage capacity

per unit weight as well as improved lithium diffusion through the nanostructured silicon thin film layer.

Another advantage of the rechargeable battery 1 is that the plurality of silicon columns 12 and interfaces 14 therebetween allow for volumetric changes of the nanostructured silicon thin film layer when lithium ions are absorbed and released. More precisely, the interfaces 14 or spaces between the plurality silicon columns 12 enable stress relaxation during volumetric changes thereof during lithium ion (de)intercalation, so that cracking and pulverization of the nanostructured silicon thin film layer is reduced. Charge retention of up to 85% after 100 recharging cycles of the rechargeable battery 1 is feasible.

In an embodiment, the nanostructured silicon thin film layer (i.e. the anode layer 6) has a porosity of about 30% to about 60%, which is defined by a spatial distribution and arrangement of the plurality of silicon columns 12 across the anode layer 6. The porosity of the nanostructured silicon thin film layer provides improved diffusion of lithium ions throughout the silicon anode layer 6 and to facilitate volumetric changes and stress relaxation of the silicon anode layer 6 during the (de)intercalation process. The porosity value has been deduced from optical measurements for samples of nanostructured silicon thin films, in accordance with a method described by Braun in Thin Solid Films, vol. 496 (2004) p505.

In most embodiments the spatial distribution or arrangement of the plurality of silicon columns 12 is a substantially random distribution across the anode layer 6. That is, the plurality of silicon columns 12 is randomly distributed in lateral sense with respect to the planar direction, e.g. parallel to the anode surface 10. This random distribution of silicon columns 12 and interfaces 14 there between does not only provide improved lithium diffusion and stress relieve within the nanostructured silicon thin film layer during volumetric changes thereof, but the random distribution of the plurality of silicon columns 12 and interfaces 14 also facilitates the manufacturing process as the spatial distribution need not be actively controlled. In essence the nanostructured silicon thin film layer is a self-organized nanostructured silicon thin film layer.

In an embodiment, the interfaces 14 form diffusion paths for lithium ions during intercalation and de-intercalation. The diffusion paths provided by the interfaces 14 improve accessibility for lithium ions to each of the plurality of silicon columns 12 and

to be absorbed and released by it during (de)intercalation. Consequently, energy storage capacities of up to 4000 mAh/g are achievable. The interfaces 14 also reduce stress and strain within the plurality of silicon columns 12 by allowing for volumetric changes thereof upon lithium ion insertion and extraction, thereby minimizing cracking and pulverization of the nanostructured silicon thin film layer.

In advantageous embodiments each one of the plurality of silicon columns 12 is elongated in the perpendicular direction perpendicular to the anode surface that interfaces with the electrolyte layer. In this embodiment the plurality of silicon columns 12 can be envisaged as nanostructured elongated columns 12 or posts 12 arranged perpendicular or substantially perpendicular to the anode surface 10 and/or the substrate 5 of the anode layer 6. The elongated shape of the plurality of silicon columns 12 increases the freedom for volumetric changes of each of the silicon columns 12 during (de)intercalation of lithium ions. For example, each of the silicon columns 12 has more freedom to expand or contract laterally with respect to the perpendicular direction, so that cracking and pulverization of the plurality of silicon columns 12 is reduced and hence capacity fading is kept to a minimum.

In a specific embodiment, the plurality of silicon columns 12 have a length (or height) in the perpendicular direction of about 3 μm to about 8 μm , thereby providing a sufficiently thin silicon anode layer 6 that has an improved resistance to cracking and pulverization over multiple recharging cycles.

In a further specific embodiment, each one of the plurality of silicon columns 12 has an average footprint of about 0.25 μm^2 to about 0.5 μm^2 along the anode surface of the nanostructured silicon thin film layer, which provides an improved aspect ratio between a base width and length/height in the perpendicular direction of each of the silicon columns 12, which further facilitates volumetric changes during lithium (de)intercalation hence reduced cracking and pulverization of each of the silicon columns 12.

In an advantageous embodiment, the nanostructured silicon thin film layer is arranged on a substrate comprising a metallic conductor layer, e.g. copper, nickel, which provide excellent electrical conductivity.

In light of the present invention, various lithium salt compounds can be used in conjunction with the nanostructured silicon thin film layer. For example, in a group of embodiments the lithium salt compound may comprise LiCoO_2 ("Li-cobalt"), LiMn_2O_4

(“Li-manganese spinel”, “LMO”), LiFePO_4 (“Li-phosphate”), LiNiMnCoO_2 (“NMC”), LiNiCoAlO_2 (“NCA”) or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (“Li-titanate”, “LTO”). Each of these lithium salt compounds can be found in particular applications, ranging from electric vehicle (EV) batteries to portable computer batteries, cell phone batteries and the like. The rechargeable battery 1 of the present invention can therefore be used in existing battery configurations of commercial products.

In a further aspect, the present invention relates to a method of manufacturing a rechargeable battery. Reference is made to the Figures 1, 2 and 3.

According to the invention, a method is provided for manufacturing a rechargeable battery 1 comprising at least an electrolyte layer 2, a cathode layer 4 and an anode layer 6. The method comprises the steps of forming on a substrate 5 a nanostructured silicon thin film layer as an anode layer 6, wherein the forming process is configured to create the nanostructured silicon thin film layer comprising a plurality of adjacent silicon columns 12 (i.e., silicon based columns). As explained above, a nanostructured silicon thin film layer is capable of providing a significantly higher, e.g. 10 fold, energy storage capacity than prior art graphite anodes.

During the formation process, the silicon-based columns 12 are extending perpendicular to a surface of the nanostructured thin film layer. The plurality of silicon columns 12 is arranged adjacent to each other while separated by interfaces 14 extending in the perpendicular direction, with the separation distance of the interfaces being substantially parallel to the surface of the nanostructured thin film layer. Once formed, the plurality of silicon columns 12 comprise amorphous silicon (am-Si), as verified by structural analysis of the thin film material.

As mentioned hereinbefore, the term amorphous silicon should be construed as comprising proto-crystalline silicon, thus wherein amorphous silicon may comprise a small fraction of nano-crystalline silicon up to about 30% of the nanostructured silicon thin film layer. Further, the term “silicon” should also be construed as comprising silicon-based materials, i.e., silicon alloys.

The method further comprises providing a lithium salt compound as the electrolyte layer 2 and arranging the electrolyte layer 2 between a cathode surface 8 of the cathode layer 4 and an anode surface 10 of the anode layer 6.

An advantage of the method is that the plurality of silicon columns 12 are formed in a self organising fashion and randomly distributed across the substrate 5, so

it is not necessary to actively steer or control the column formation. The method of the present invention is therefore a one-step, self organising, spontaneous process for forming a nanostructured silicon thin film layer without pre- or post-method steps. As a result the method is readily adapted to produce silicon based anodes at industrial levels for commercialization.

Another advantage of the method is that a variety of substrates 5 can be used for forming the nanostructured silicon thin film layer. In most embodiments, however, the substrate 5 will be a metallic substrate or metallic substrate layer (e.g. copper, nickel) in view of good electrical conductivity thereof.

In an embodiment, the forming process comprises deposition of the anode layer 6 by Plasma Enhanced Chemical Vapour Deposition (PECVD), thereby allowing for deposition of a nanostructured thin film anode layer having a thickness of 0.05 μm to 10 μm .

In a further embodiment, the PECVD process comprises the use of a microwave plasma of a mixture of silane, SiH_4 , and hydrogen, H_2 . The use of microwave frequencies reduces ion bombardment of anode growth zones on the substrate during the forming process, so that growth rates of the anode layer 6 are increased.

In an even further embodiment, the mixture of SiH_4 and H_2 further comprises argon (Ar). Using such a mixture allows for a sustained plasma at lower pressures and to promote self organized growth of the nanostructured silicon thin film layer, i.e. the plurality of silicon columns 12 and column boundaries, i.e., interfaces 14 there between. Here, self organized growth means that the formation of the plurality of silicon columns 12 and interfaces 14 there between occurs spontaneously. The plurality of silicon columns 12 are deposited in a substantially random fashion across and along the substrate 5, thus forming a substantially random arrangement. The self organized formation of the plurality of silicon columns 12 can be viewed as a one step manufacturing process, circumventing pre- and post-treatment of the substrate 5 or deposited silicon anode layer 6.

Additionally, the formation of the nanostructured thin film layer comprises addition of a doping pre-cursor to obtain a doped nanostructured silicon thin film layer of either n-type or p-type in dependence of the precursor type. In an embodiment, the precursor is a gaseous species added to the mixture of silane and hydrogen.

In many embodiments the PECVD process is a low-pressure PECVD process. For example, in an embodiment the low-pressure PECVD process comprises pressures above 0.15 mbar, so that a sustainable plasma can be maintained when a mixture of silane, SiH_4 , and hydrogen, H_2 , is used. In another embodiment the low-pressure
5 PECVD process comprises pressures below 0.15 mbar when the mixture of silane, SiH_4 , and hydrogen, H_2 , further comprises argon (Ar).

In a further embodiment, the PECVD process is a microwave PECVD process. To allow for large area production of silicon anode layers 6, in an advantageous embodiment the microwave plasma is created by an elongated antenna wire, of which
10 each end of the wire is coupled to a microwave generator. The elongated antenna wire provides a substantially linear and uniform field of microwave radiation in the plasma reactor during the formation process, so that a more uniform deposition of the plurality of silicon columns is achieved over a large area. In an embodiment the length of the antenna wire is 50 cm or more, e.g. 60 cm. The length of the antenna wire directly
15 influences the surface produced of the nanostructure silicon thin film layer. Increasing the length of the antenna wire typically increases the achievable surface area of the nanostructured silicon thin film layer that can be manufactured.

Without any limitation of the inventive concept and without being bound to any theory on the deposition mechanism, it is considered that according to an embodiment
20 the method for formation of the nanostructured silicon thin film, is configured to provide growth conditions of the silicon thin film where the deposited silicon atoms experience a relatively low surface mobility resulting in the typical columnar structure of the nanostructured silicon thin film.

The present invention embodiments have been described above with reference
25 to a number of exemplary embodiments as shown in and described with reference to the drawings. Modifications and alternative implementations of some parts or elements are possible, and are included in the scope of protection as defined in the appended claims.

CONCLUSIES

1. Oplaadbare batterij omvattend ten minste een elektrolyt laag (2), een kathode laag (4) en een anode laag (6); waarbij de elektrolyt laag (2) omvat,
 5 een lithiumzoutverbinding gerangschikt tussen een kathode oppervlak (8) van de kathode laag (4) en een anode oppervlak (10) van de anode laag (6); waarbij de anode laag (6) een van een nanostructuur voorziene dunne film laag is die een veelheid naast elkaar liggende kolommen (12) omvat, waarbij de
 10 kolommen (12) zich uitstrekken in een loodrechte richting vanaf het anode oppervlak (10), waarbij de naast elkaar gelegen kolommen van elkaar gescheiden zijn door interfaces (14) die zich uitstrekken in de loodrechte richting, waarbij de kolommen (12) silicium omvatten en een amorfe structuur hebben.
- 15 2. Oplaadbare batterij volgens conclusie 1, waarbij de kolommen bestaan uit amorf silicium.
3. Oplaadbare batterij volgens conclusie 1, waarbij de kolommen een silicium legering omvatten.
 20
4. Oplaadbare batterij volgens conclusie 3, waarbij de silicium legering een amorfe structuur heeft.
5. Oplaadbare batterij volgens conclusie 3, waarbij de kolommen ten minste een
 25 materiaal omvatten dat gekozen is uit amorf silicium en een amorfe silicium legering.
6. Oplaadbare batterij volgens conclusie 3, waarbij de kolommen amorf silicium en een nano-kristallijne silicium legering omvatten.
 30
7. Oplaadbare batterij volgens willekeurig welke van de conclusies 1 - 6, waarbij de silicium legering wordt gekozen uit een groep van legeringen omvattend

Si-C, Si-N, Si-Ge, Si-Ag, Si-Sn.

8. Oplaadbare batterij volgens willekeurig welke van de conclusies 1 - 7, waarbij de amorfe structuur tot 30% van de nano-kristallijne structuur bevat.
- 5 9. Oplaadbare batterij volgens willekeurig welke van de conclusies 1 - 8, waarbij de van een nanostructuur voorziene dunne film laag een porositeit heeft van ongeveer 30% tot ongeveer 60%.
- 10 10. Oplaadbare batterij volgens willekeurig welke van de conclusies 1 - 9, waarbij de interfaces (14) diffusiepaden voor Li ionen vormen gedurende intercalatie en deintercalatie.
- 15 11. Oplaadbare batterij volgens willekeurig welke van de conclusies 1 - 10, waarbij de kolommen langwerpig zijn in de loodrechte richting.
12. Oplaadbare batterij volgens conclusie 11, waarbij de kolommen een lengte in de loodrechte richting hebben van ongeveer 3 μm tot ongeveer 8 μm .
- 20 13. Oplaadbare batterij volgens conclusie 11 of conclusie 12, waarbij de kolommen een gemiddelde oppervlakbedekking hebben van ongeveer 0.25 tot ongeveer 0.5 μm^2 , langs het oppervlak van de van een nanostructuur voorziene dunne film laag.
- 25 14. Oplaadbare batterij volgens willekeurig welke van de voorgaande conclusies 1 - 13, waarbij de van de nanostructuur voorziene dunne film laag is aangebracht op een substraat dat een laag van een metallische geleider omvat.
15. Werkwijze voor het vervaardigen van een oplaadbare batterij omvattend ten minste een elektrolyt laag (2), een kathode laag (4) en een anode laag (6), waarbij de werkwijze omvat de stappen van:
het vormen op een substraat van een van een nanostructuur voorziene dunne film laag als de anode laag (6), waarbij het vormingsproces is geconfigureerd
- 30

voor het vormen van de van de nanostructuur voorziene dunne film laag welke een veelheid naast elkaar gelegen kolommen (12) omvat, waarbij de kolommen (12) zich uitstrekken in een loodrechte richting vanaf het substraat en zijn gerangschikt naast elkaar maar onderwijl van elkaar gescheiden door interfaces (14) die zich uitstrekken in de loodrechte richting, waarbij de veelheid kolommen (12) silicium omvatten en een amorfe structuur hebben; waarbij de werkwijze verder omvat het verschaffen van een lithiumzoutverbinding als de elektrolyt laag (2); en het aanbrengen van de elektrolyt laag (2) tussen een kathode oppervlak (8) van de kathode laag en een anode oppervlak (10) van de anode laag (6).

16. Werkwijze volgens conclusie 15, waarbij de kolommen bestaan uit amorf silicium.
- 15 17. Werkwijze volgens conclusie 15 of conclusie 16, waarbij de kolommen een silicium legering omvatten.
18. Werkwijze volgens willekeurig welke van de conclusies 15 - 17, waarbij de kolommen ten minste een materiaal omvatten dat gekozen is uit amorf silicium en een amorfe silicium legering.
- 20 19. Werkwijze volgens willekeurig welke van de conclusies 15 - 18, waarbij de kolommen amorf silicium en een nano-kristallijne silicium legering omvatten.
- 25 20. Werkwijze volgens willekeurig welke conclusies 15 - 19, waarbij het vormingsproces depositie van de anode laag door PECVD omvat.
21. Werkwijze volgens conclusie 20, waarbij het PECVD proces het gebruik van een microgolfplasma van een mengsel omvattend silaan, SiH_4 , en waterstof, H_2 omvat.
- 30 22. Werkwijze volgens conclusie 21, waarbij het mengsel van SiH_4 en H_2 verder een legeringvormende component, voor het vormen van de silicium legering

omvat.

23. Werkwijze volgens willekeurig welke van de conclusies 21 - 22, waarbij de vorming van de van de nanostructuur voorziene dunne film laag het toevoegen van een doopstofprecursor van ofwel n-type ofwel p-type voor het doteren van de van de nanostructuur voorziene dunne film laag als een ofwel n-type ofwel p-type geleidende laag omvat.
5
24. Werkwijze volgens willekeurig welke van de conclusies 21 - 23, waarbij het mengsel van SiH_4 en H_2 voorts argon, Ar omvat.
10
25. Werkwijze volgens willekeurig welke van de conclusies 20 - 24, waarbij het microgolflasma wordt gevormd door een langwerpige antennedraad, waarvan elk draaduiteinde is gekoppeld aan een microgolfgenerator.
15
26. Werkwijze volgens willekeurig welke van de conclusies 20 - 25, waarbij het PECVD proces een lage-druk PECVD proces is.
27. Werkwijze volgens willekeurig welke van de conclusies 20 - 26, waarbij het substraat een laag van een metallische geleider is.
20

Fig. 1

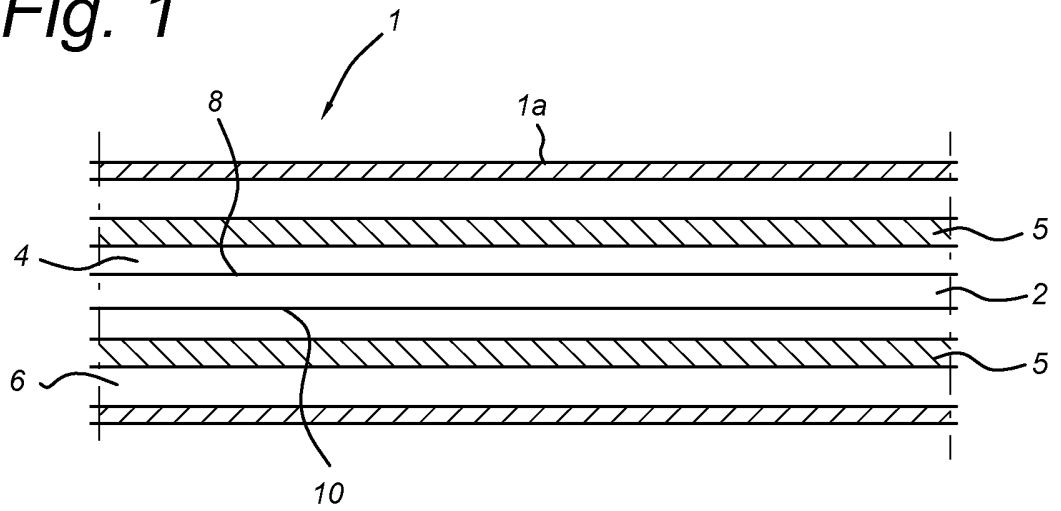


Fig. 2

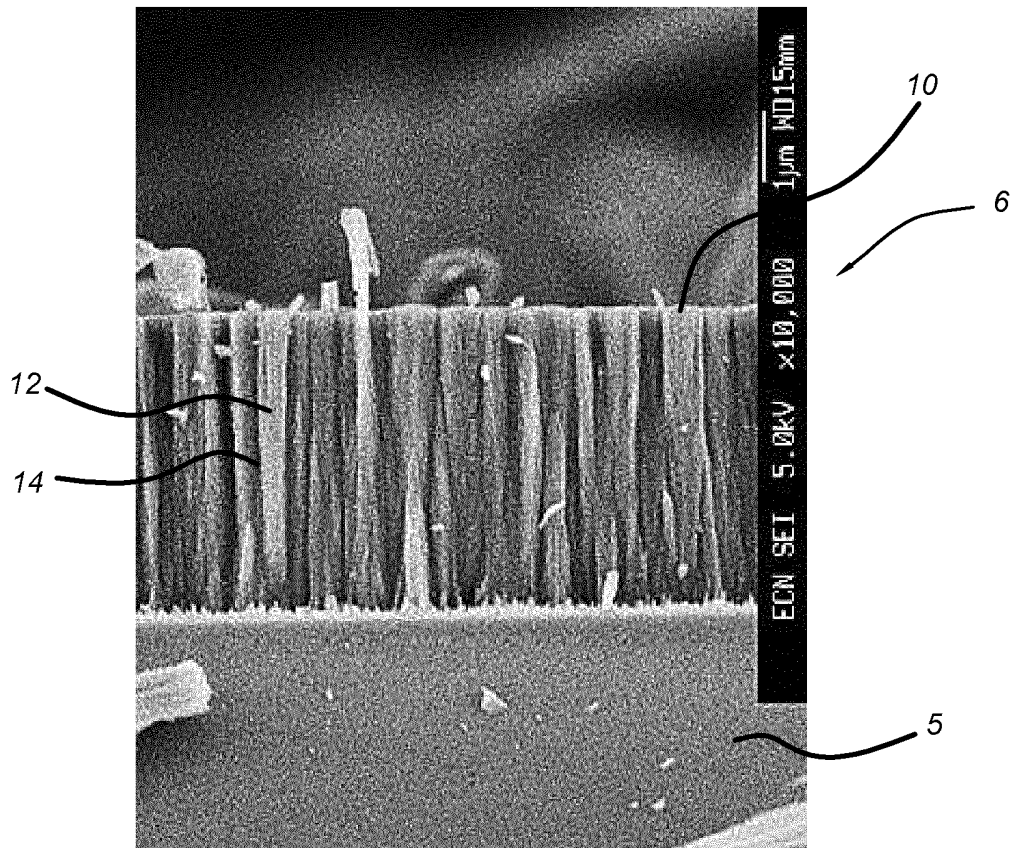
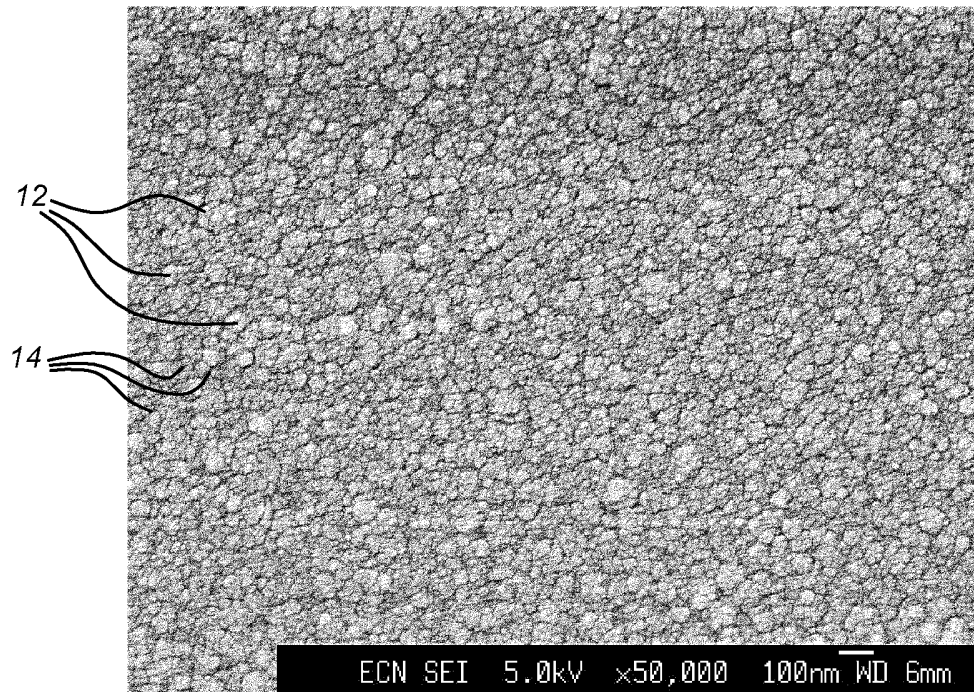


Fig. 3



ABSTRACT

Rechargeable battery comprising at least an electrolyte layer (2), a cathode layer (4) and an anode layer (6); the electrolyte layer (2) comprising a lithium salt compound
5 arranged between a cathode surface (8) of the cathode layer (4) and an anode surface (10) of the anode layer (6). The anode layer (6) is a nanostructured silicon thin film layer comprising a plurality of silicon columns (12), wherein the silicon columns (12) are directed in a first direction perpendicular or substantially perpendicular to the anode surface (10) of the silicon thin film layer. The silicon columns are arranged adjacent to
10 each other while separated by grain-like column boundaries (14) running along the first direction. The silicon columns (12) comprise amorphous silicon.

[Figure 1]

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE Nederlands aanvraag nr. 2014588	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE P6053881NL
Indieningsdatum 07-04-2015	Ingeroepen voorrangsdatum
Aanvrager (Naam) Stichting Energieonderzoek Centrum Nederland	
Datum van het verzoek voor een onderzoek van internationaal type 04-07-2015	Door de instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. SN 64441
I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)	
Volgens de internationale classificatie (IPC)	
H01M4/04 H01M4/36	H01M4/134 H01M4/38
H01M4/1395 H01M10/0525	
II. ONDERZOCHE GEBIEDEN VAN DE TECHNIEK	
Onderzochte minimumdocumentatie	
Classificatiesysteem	Classificatiesymbolen
IPC	H01M
Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen	
III.	☐ GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES (opmerkingen op aanvullingsblad)
IV.	☐ GEBREK AAN EENHEID VAN UITVINDING (opmerkingen op aanvullingsblad)

**ONDERZOEKSRAPPORT BETREFFENDE HET
RESULTAAT VAN HET ONDERZOEK NAAR DE STAND
VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE**

Nummer van het verzoek om een onderzoek naar
de stand van de techniek

NL 2014588

A. CLASSIFICATIE VAN HET ONDERWERP

INV. H01M4/04 H01M4/134 H01M4/1395 H01M4/36 H01M4/38
H01M10/0525

ADD.

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimum documentatie (klassificatie gevolgd door classificatiesymbolen)

H01M

Onderzochte andere documentatie dan de minimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)

EPO-Internal, WPI Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie *	Gesleekte documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie n°
X	LI-FENG CUI ET AL: "Crystalline-Amorphous Core-Shell Silicon Nanowires for High Capacity and High Current Battery Electrodes", NANO LETTERS, AMERICAN CHEMICAL SOCIETY, US, deel 9, nr. 1, 1 januari 2009 (2009-01-01) , bladzijden 491-495, XP007913274, ISSN: 1530-6984, DOI: 10.1021/NL8036323 [gevonden op 2008-12-23] * bladzijde 492, kolom 2, alinea 1 - bladzijde 493, kolom 2, alinea 2 *	1-6,10, 11,14-27
X A	US 2015/004485 A1 (CHEN ZHAOHUI [US] ET AL) 1 januari 2015 (2015-01-01) * alinea [0022] - alinea [0068]; figuur 3 * ----- -/-	1-11, 13-27 12



Verdere documenten worden vermeld in het vervolg van vak C.



Leden van dezelfde octroofamilie zijn vermeld in een bijlage

*** Speciale categorieën van aangehaalde documenten**

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"C" in de octrooiaanvraag vermeld

"E" eerdere octroop(aanvraag), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermeldde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorafgedatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorafgedatum gepubliceerde literatuur die niet bezwaarlijk is voor de octrooiaanvraag, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere gesleekte literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"Z" lid van dezelfde octroofamilie of overeenkomstige octroopublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid

11 december 2015

Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type

Naam en adres van de instantie

European Patent Office, P.O. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

De bevoegde ambtenaar

Barenbrug-van Druten

**ONDERZOEKSRAPPORT BETREFFENDE HET
RESULTAAT VAN HET ONDERZOEK NAAR DE STAND
VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE**

Nummer van het verzoek om een onderzoek naar
de stand van de techniek

NL 2014588

C (Verzoek) VAN BELANG GEACHTE DOCUMENTEN

Categorie *	Geëciteerde documenten, eventueel met aanduiding van specifiek van belang zijnde passages	Van belang voor conclusie nr.
X	WO 2011/094642 A1 (ILLUMINEX CORP [US]; CARACCILO ROBERT; HABIB YOUSSEF) 4 augustus 2011 (2011-08-04) * alinea [0002] - alinea [0032]; figuur 2 *	1,2,4,5, 8-16,18, 20-27
X	----- EP 2 372 751 A1 (SAMSUNG ELECTRONICS CO LTD [KR]; UNIV DONGGUK IND ACAD COOP [KR]) 5 oktober 2011 (2011-10-05) * alinea [0032] - alinea [0042] *	1,2,5, 9-12, 14-17
A	----- US 2009/169725 A1 (ZHANG ARUNA [US] ET AL) 2 juli 2009 (2009-07-02) * alinea [0119] - alinea [0120] *	1-27

**ONDERZOEKSRAPPORT BETREFFENDE HET
RESULTAAT VAN HET ONDERZOEK NAAR DE STAND
VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE**
informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar
de stand van de techniek
NL 2014568

In het rapport genoemd octrooigezinslid	Datum van publicatie	Overeenkomstig(e) geschrift(en)	Datum van publicatie		
US 2015004485	A1	01-01-2015	US 2015004485 A1	01-01-2015	
		WO 2014210015	A1	31-12-2014	
WO 2011094642	A1	04-08-2011	US 2011189510	A1	04-08-2011
			US 2012034524	A1	09-02-2012
			WO 2011094642	A1	04-08-2011
EP 2372751	A1	05-10-2011	CN 102234111	A	09-11-2011
			EP 2372751	A1	05-10-2011
			JP 2011219355	A	04-11-2011
			KR 20110111105	A	10-10-2011
			US 2011240954	A1	06-10-2011
US 2009169725	A1	02-07-2009	US 2009169725	A1	02-07-2009
			US 2009169996	A1	02-07-2009

WRITTEN OPINION

File No. SN64441	Filing date (day/month/year) 07.04.2015	Priority date (day/month/year)	Application No. NL2014588
International Patent Classification (IPC) INV. H01M4/04 H01M4/134 H01M4/1395 H01M4/36 H01M4/38 H01M10/0525			
Applicant Stichting Energieonderzoek Centrum Nederland			

This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☒ Box No. VII Certain defects in the application
- ☐ Box No. VIII Certain observations on the application

	Examiner Barenbrug-van Druten
--	---

WRITTEN OPINION

Application number
NL2014588

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:
 - a. type of material:
 - ☐ a sequence listing
 - ☐ table(s) related to the sequence listing
 - b. format of material:
 - ☐ on paper
 - ☐ in electronic form
 - c. time of filing/furnishing:
 - ☐ contained in the application as filed.
 - ☐ filed together with the application in electronic form.
 - ☐ furnished subsequently for the purposes of search.
3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes: Claims	25, 26
	No: Claims	1-24, 27
Inventive step	Yes: Claims	
	No: Claims	1-27
Industrial applicability	Yes: Claims	1-27
	No: Claims	

2. Citations and explanations

see separate sheet

WRITTEN OPINION

Application number
NL2014588

Box No. VII Certain defects in the application

see separate sheet

1 **Re Item V**

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1.1 Reference is made to the following documents:

- D1 LI-FENG CUI ET AL: "Crystalline-Amorphous Core-Shell Silicon Nanowires for High Capacity and High Current Battery Electrodes", NANO LETTERS, AMERICAN CHEMICAL SOCIETY, US, deel 9, nr. 1, 1 januari 2009 (2009-01-01), bladzijden 491-495, XP007913274, ISSN: 1530-6984, DOI: 10.1021/NL8036323 [gevonden op 2008-12-23]
- D2 US 2015/004485 A1 (CHEN ZHAOHUI [US] ET AL) 1 januari 2015 (2015-01-01)
- D3 WO 2011/094642 A1 (ILLUMINEX CORP [US]; CARACCILO ROBERT; HABIB YOUSSEF) 4 augustus 2011 (2011-08-04)
- D4 EP 2 372 751 A1 (SAMSUNG ELECTRONICS CO LTD [KR]; UNIV DONGGUK IND ACAD COOP [KR]) 5 oktober 2011 (2011-10-05)
- D5 US 2009/169725 A1 (ZHAMU ARUNA [US] ET AL) 2 juli 2009 (2009-07-02)

1.2 The present application does not meet the criteria of patentability, because the subject-matter of claim 1 is not new.

D1 discloses (see page 492-page 493): Oplaadbare batterij omvattend ten minste een elektrolyt laag, een kathode laag en een anode laag; waarbij de elektrolyt laag omvat een lithiumzoutverbinding gerangschikt tussen een kathode oppervlak van de kathode laag en een anode oppervlak van de anode laag; waarbij de anode laag een van een nanostructuur voorziene dunne film laag is die een veelheid naast elkaar liggende kolommen omvat, waarbij de kolommen zich uitstrekken in een loodrechte richting vanaf het anode oppervlak, waarbij de naast elkaar gelegen kolommen van elkaar gescheiden

zijn door interfaces die zich uitstrekken in de loodrechte richting, waarbij de kolommen silicium omvatten en een amorfe structuur hebben. The method of claim 15 is also disclosed.

The subject-matter of dependent claims 2-5,10,11,14-24 and 27 is also not new in view of document D1 (see pages 492-492).

- 1.3 The subject-matter of claims 1-5,7,10,11,13-18 and 27 is further not new in view of document D2 (see paragraphs 22-68 and figure 3).
- 1.4 The subject-matter of claims 1, 2, 4, 5, 8-16, 18, 20 and 27 is further not new in view of document D3 (see paragraphs 2-32 and figure 2).
- 1.5 The subject-matter of claims 1, 2, 5, 9-12, 14-17 is further not new in view of document D4 (see paragraphs 32-42)

2 Re Item VII

Certain defects in the application

- 2.1 Independent claim 1 is not in the two-part form, which in the present case would be appropriate, with those features known in combination from the prior art being placed in the preamble and the remaining features being included in the characterising part.
- 2.2 The relevant background art disclosed in D1-D5 is not mentioned in the description, nor are these documents identified therein.