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(54) Title: PROCESS FOR FABRICATING NANOWIRE ARRAYS

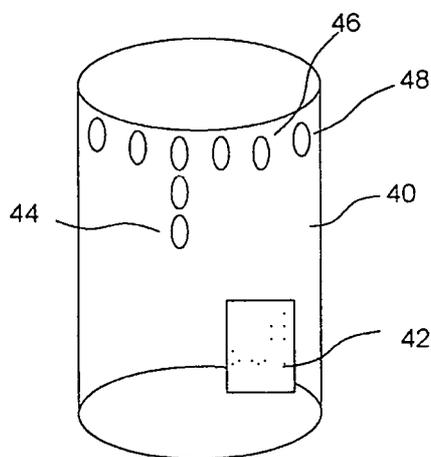


FIG. 3

(57) Abstract: A process is provided for etching a silicon-containing substrate to form nanowire arrays. In this process, one deposits nanoparticles and a metal film onto the substrate in such a way that the metal is present and touches silicon where etching is desired and is blocked from touching silicon or not present elsewhere. One submerges the metalized substrate into an etchant aqueous solution comprising HF and an oxidizing agent. In this way arrays of nanowires with controlled diameter and length are produced.



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PROCESS FOR FABRICATING NANOWIRE ARRAYS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. Provisional Applications Nos. 61/044,573, filed April 14, 2008, and 61/141,082, filed December 29, 2008. These applications are incorporated by reference herein.

TECHNICAL FIELD

[0002] This application pertains to the field of nanotechnology.

BACKGROUND OF THE INVENTION

[0003] The ability to structure and pattern silicon is important for many applications. There has been particular interest in patterning silicon to make nanostructures. Relevant information regarding silicon fabrication processes known to those of skill in the art can be found, for example, in Sami Franssila, *Introduction to Microfabrication* (John Wiley & Sons, 2004), and the references cited there.

[0004] Semiconductor nanowires have become the focal point of research over the last decade due to their interesting physical, chemical and biological properties. There is particular interest surrounding silicon nanowires, as silicon is one of the most abundant materials in the earth's crust and has become a cornerstone for many of the electronic, optoelectronic, electro-chemical and electro-mechanical devices upon which designs are based.

[0005] Today, many nanosystems are not utilized commercially due to the large cost associated with fabrication, and limitations in the scalability of nanowire synthesis. Nanowires have been grown bottom up using molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), and physical vapor deposition (PVD). They have also been fabricated top-down using techniques like reactive ion etching (RIE) and inductively coupled plasma (ICP). These systems require high temperature and/or low pressure which is largely responsible for the high cost. A push towards solution based techniques that can be operated in ambient conditions is important given their low cost, simplicity of design and ease of utilization.

[0006] Recent work has demonstrated the fabrication of silicon nanowires using a solution made up of a metal salt and a strong acid (typically AgNO_3 and HF). (See reference (a).) By controlling the concentrations of each component in solution, silicon

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can be etched normal to the plane of the wafer forming vertically aligned silicon nanowires with an average diameter of 150nm and a diameter range from 20-300nm. Through the realization that silver is precipitating out of solution and catalyzing the silicon etch, the technique has been modified to incorporate the addition of H_2O_2 into the chemical bath and Ag metal directly deposited onto silicon. Polystyrene spheres of uniform dimensions were dispersed prior to the deposition of the Ag in order to use them as an etch mask and define the nanowire. (See reference (e).) As a result, ordered arrays of silicon nanowires with a homogeneous diameter and length were demonstrated.

[0007] The ultimate diameter achieved with this technique has been limited. The ability to achieve sub-100 nm dimensions is of value to a variety of electronic, optoelectronic, electrochemical and electromechanical applications. For example, it is within the sub-100 nm range that silicon begins to demonstrate novel properties distinguishable from the properties of bulk silicon. In addition, an increase in surface area at the low nanometer scale is of value.

SUMMARY OF THE INVENTION

[0008] A process is provided for etching a silicon-containing substrate to form nanowire arrays. In this process, one deposits nanoparticles and a metal film onto the substrate in such a way that the metal is present and touches silicon where etching is desired and is blocked from touching silicon or not present elsewhere. One submerges the metallized substrate into an etchant aqueous solution comprising HF and an oxidizing agent. In this way arrays of nanowires with controlled diameter and length are produced.

BRIEF DESCRIPTION OF THE FIGURES

[0009] FIG. 1 depicts the result of using an embodiment of the invention to obtain nanowires with diameters that ranged from 12-70 nm.

[00010] FIG. 2 depicts the result of using the alternative embodiment described below in part B to obtain nanowires.

[00011] FIG. 3 depicts schematically a setup for practicing processes of the invention, using oxygen as an oxidizer.

[00012] FIG. 4 depicts the result of using metal enhanced etching of silicon to obtain microstructuring on a silicon wafer. Unintentional wires were formed inside the trenches.

DETAILED DESCRIPTION OF THE INVENTION

[00013] In an aspect of the invention, a process is provided for etching a silicon-containing substrate to form nanostructures. In this process, one deposits and patterns a metal film onto the substrate in such a way that the metal is present and touches silicon where etching is desired and is blocked from touching silicon or not present elsewhere. One submerges the metallized substrate into an etchant aqueous solution comprising about 4 to about 49 weight percent HF and an oxidizing agent.

[00014] In a process as described above, to achieve sub-100 nm nanowires, one may use sub-100 nm nanoparticles to block the silver from the silicon. The nanoparticles may be made of a variety of substances, for example silicon dioxide, iron oxide, or polymers.

[00015] A. FIRST EXEMPLARY PROCESS

[00016] An exemplary process utilizes the spinning of SiO₂ nanoparticles well dispersed in an isopropanol solution (5wt% SiO₂ in IPA) that ranged in particle size from 12-30nm at 4000RPM. Subsequent to spin-coating, the samples were heated at elevated temperatures resulting in solvent evaporation. Once the samples were dry, 40 nm of Ag was sputter deposited on top in order to coat the SiO₂ nanoparticles as well as the bare silicon spaces in between. The samples were dipped into an HF/H₂O₂ solution for a period of 10 minutes. The etching reaction commenced at the Ag/Si interface and the nanoparticles acted as a barrier by which to mask and define the nanostructure. The dimensions of the nanoparticles, which are selected per the desired application, influence the dimensions and the shape of the resulting one-dimensional nanostructure. Some agglomeration occurred between the SiO₂ nanoparticles resulting in wire dimensions on the order of a single agglomerate. By selecting the concentration of particles in solution as well as the method for depositing/spin coating the particles, it is possible to limit agglomeration resulting in nanowires that ranged from 12-70 nm. A result is depicted in FIG. 1.

[00017] B. FIRST ALTERNATIVE

[00018] In a variant on the process described above, one uses iron oxide nanoparticles (5-10nm) with surfaces that have been pretreated with oleic acid and dispersed in chloroform. This surface treatment was done in order to prevent agglomeration and maintain a stable nanoparticle suspension. In this situation it was not necessary to spin coat. Deposition of the nanoparticles onto the silicon substrate was achieved by applying a few drops of the solution to the surface under static conditions (no spinning). Rapid

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evaporation at room temperature resulted in a monodispersed layer of the iron oxide particles on the silicon substrate with little to no agglomeration. Without wishing to be bound by theory, it is believed that the monodispersed layer resulted at least in part from the pre-tailored surface tension properties and the high vapor pressure of the solvent.

[00019] In this alternative process, Ag was sputter deposited on the surface and the substrate to coat the iron oxide particles and the spaces in between. The sample was dipped into a similar HF/H₂O₂ solution in order to begin the etching reaction and form the nanowires. An example of the result is seen in FIG. 2. There is some bundling that occurs due to the drying process, making it difficult to determine precisely the actual nanowire dimension. However, all of the measurable structures had a diameter less than 30nm.

[00020] C. SECOND ALTERNATIVE

[00021] In a further variation of the process, other oxidizers may be used in place of H₂O₂ in the H₂O₂-HF etchant solution. An oxidizing agent (also called an oxidant or oxidizer) is a substance that readily transfers oxygen atoms or tends to gain electrons in a redox chemical reaction. One such oxidizer is pure oxygen, which may be introduced by bubbling oxygen through the HF. Other oxidizers include: ozone, chlorine, iodine, ammonium perchlorate, ammonium permanganate, barium peroxide, bromine, calcium chlorate, calcium hypochlorite, chlorine trifluoride, chromic acid, chromium trioxide (chromic anhydride), peroxides such as hydrogen peroxide, magnesium peroxide, dibenzoyl peroxide and sodium peroxide, dinitrogen trioxide, fluorine, perchloric acid, potassium bromate, potassium chlorate, potassium peroxide, propyl nitrate, sodium chlorate, sodium chlorite, and sodium perchlorate.

[00022] It may be desirable to use a less reactive alternative oxidizer in place of H₂O₂. Comparative reactivity towards the metal deposited (e.g., silver), silicon, or silicon dioxide may be of interest in the selection of an oxidizer. Reactivity may be measured, for example, by the extent to which the reaction goes forward in a particular period of time, or by determining a reaction rate as discussed in books on physical chemistry and chemical kinetics. (See, e.g., Peter W. Atkins & Julio de Paula, *Atkins' Physical Chemistry* (8th ed. 2006), especially chapters 22 and 23.) Measurements may be made in conditions such as temperature and pressure similar to those of the etching process.

[00023] An exemplary process would be as follows:

[00024] Silicon material with a resistivity of greater than 20 ohm-cm is selected having a surface with (100), (110), (111) or any orientation available. Amorphous and/or microcrystalline material will also result in vertically oriented nanowires if one carries out the following process.

[00025] The substrate is pre-cleaned using a series of solvents by sonicating for three minutes each in acetone, methanol and then isopropyl alcohol. The substrate is then rinsed in a dump-tank of flowing deionized water (DI) for 3 minutes to remove any residue remaining from the solvent clean. The silicon is placed into a Piranha solution made up of 3 parts 96% H₂SO₄ and 1 part 30wt% H₂O₂ for 15 minutes in order to remove any additional organics and create a hydrophilic surface. The substrate is then removed from the bath and placed into a dump tank of flowing DI water again for 3 minutes to remove any residual acids. The substrate is removed and blown dry with nitrogen gas.

[00026] A colloidal suspension of 10nm iron oxide nanoparticles in chloroform is made by diluting product #SOR- 10-0050 from OceanNanotech to a concentration of 1mg/mL. The silicon wafer is coated with the iron oxide by dipping the silicon into the colloidal suspension and then removing the substrate so that the surface normal is perpendicular to the vertical direction of motion allowing the chloroform to sheet off the surface. The combination of the hydrophilic surface and the nature of the oleic acid functionalized iron oxide nanoparticles, results in a natural self-assembly that limits agglomeration and gives some reasonable spacing to the particles. The samples are then baked on an 80°C hot plate for 2 minutes and cleaned using an in-situ O₂ plasma prior to metal deposition.

[00027] In addition to iron oxide nanoparticles, 100nm polystyrene spheres have also been used successfully in this process. In this situation, a hydrophilic surface is created on the silicon substrate as described above. The polystyrene spheres (purchased from Duke Scientific Corporation) are diluted to a concentration of 1% and spun onto the substrate at 500RPM for 5 seconds followed by a ramp to 2000RPM for 40 seconds. The polystyrene spheres create a single monolayer on the surface. An O₂ plasma is used to reduce the size and spacing in the polystyrene spheres inside a plasma stripper prior to inserting the sample into the metal deposition tool (30W, 200mTorr). The sample heats up during the plasma clean, which can change the properties (or melt) the polystyrene making it difficult to continue the shrinking process. To resolve this, the polystyrene is etched using short 1 minute intervals, removing the substrate from the tool and allowing it

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to cool to room temperature prior to the next 1 minute etch. Preferably the shrinking process is done in-situ (inside the metal deposition tool) prior to metal deposition with Ar or θ_2 .

[00028] Silver (Ag) is deposited via physical vapor deposition inside a sputterer, thermal evaporator or e-beam evaporator. It is desirable that a continuous film results, where there are no breaks or cracks that would cause a portion of the film to become isolated from the remainder. As HF concentration is altered, the optimal film thickness may need to be varied.

[00029] Once the chip is coated with the appropriate film of Ag, the HF solution is seasoned before commencing the etching reaction. The concentration of HF can vary from full strength (about 49wt%) all the way down to very nominal concentrations. Initial observations have shown that the length of the resulting nanostructure increases as HF concentration is reduced. Concentrations as low as 2 wt% and below may be used. For example, a solution of 8 wt% HF may be used.

[00030] O_2 gas is flowed into the bath to create a vigorous bubbling for a period of 10 minutes. Once the bath is seasoned, the samples are submerged. At the completion of the etch, the samples are removed and put into a dump-tank of flowing DI water and blown dry with N_2 . At this point the remaining Ag on the surface can be removed with a silver etchant, for example the etchant supplied by Transene Corporation.

[00031] FIG. 3 depicts a setup for the use of oxygen gas as an oxidizer. There is a container holding HF etchant 40. In the container there is a silver/silicon substrate 42. There is an oxygen source 44 which produces oxygen bubbles such as 46 and 48. The oxygen source inlet may be placed at, above, or below the level of the substrate. With this less aggressive oxidizer, all wires were formed by the intentional nanoparticle mask that was spun on top of the surface. No defects formed in the metal film during etching were apparent.

[00032] An advantage of the processes which use alternative oxidizers is that they are able to eliminate unintentional nanowires ("grass") formed in some variants of the processes described above, while still producing the desirable sub-100nm nanowires while using a thin continuous layer of metal for catalyzed etching of silicon. FIG. 4 depicts unintentional nanowires. Avoidance of these unintentional nanowires both saves an etching step which would be used to eliminate them and also avoids the rounding of nanostructure corners and edges which would result from such an etching step.

[00033] While not wishing to be bound by theory, it is believed that some of the alternative oxidizers used in these processes of the invention do not attack the metal, or attack it to a much lesser degree than H_2O_2 . This may be a reason why processes with alternative oxidizers avoid the formation of unintentional nanowires. For this reason it may be desirable to use oxidizers known to react less readily or at a lower rate with the metal than H_2O_2 does.

[00034] In order to avoid unintentional wires, it is desirable that the metal film be free of small unintentional holes and be deposited on a clean silicon surface free of oxide.

[00035] A further advantage of the processes of the invention is that they are extendable to specified crystallographic directions. With at least some processes of the invention, irrespective of the crystal orientation of the silicon surface, the nanowires will be etched at least approximately perpendicular to that surface. In order to achieve this, it is desirable that the metal film has no breaks or cracks that would cause a portion of the film to become isolated from the remainder. It is also desirable that the metal film has sufficient adhesion and is deposited on a clean silicon surface. Desirable angles between nanowire axes and a vector normal to the substrate may be, for example, less than about 0.25 degrees, about 0.5 degrees, about 1 degree, or about 2 degrees.

[00036] With processes of the invention, it is possible to make wires which have a noticeable taper that results in the wire diameter increasing slightly as the etch progresses. The taper has been found to increase with HF concentration. For some applications, the taper may not be desirable. For photovoltaic applications, however, a taper may be beneficial. For example, with a slight taper, free carriers in the nanowire will bounce off the edges of the wire and thus tend propagate downward to the substrate. If the p-n junction of the photovoltaic cell is in the substrate rather than in the nanowires, this increased diffusion towards the substrate may be expected to increase the cell efficiency. Desirable taper angles might be, for example, no more than about 0.5 degrees, about 1 degree, about 2 degrees, or about 4 degrees, or in a range between about 0.5 degrees and about 1 degree, about 2 degrees, or about 4 degrees.

[00037] Using processes of the invention it is possible to achieve nanowire diameters which are on average (e.g., have a mean or median) below about 150 nm, below about 125 nm, below about 100 nm, below about 70 nm, or below about 50 nm. Small nanowires are important in certain applications, such as where the small size changes the band structure of the silicon. It may be desired, for example, that a majority, or at least

about 75%, or about 90%, or about 95% of the nanowires have diameters less than a selected dimension such as those indicated above.

[00038] D. APPLICATIONS

[00039] Processes of the invention may be applied to structuring silicon for optoelectronic devices (see reference (i)). They may be employed in devices that utilize the photoelectric or photovoltaic effect, for example solar cells (see, e.g., references (j) and (k)), photodetectors, photodiodes (see reference (a)), phototransistors, photomultipliers and integrated optical circuits. Silicon nanowire arrays or individual nanowires fabricated via this process can be utilized within each of these applications.

[00040] Processes of the invention may be employed to produce devices made out of or comprising polycrystalline silicon. The invention encompasses processes which can be used with any crystalline orientation of silicon. Such processes can be used to texture the surface of and/or form nanowires in polysilicon. Polysilicon is a cheaper material than crystalline silicon, but it is typically more difficult to texture and structure than single crystal silicon due to the random orientation of the grains. The processes of the invention can likewise be used to form nanowires in amorphous silicon.

[00041] Arrays of silicon nanowires can be used in applications where the silicon will be subjected to stress or strain where the nanostructure is able to absorb and relax this stress or strain. For example, nanowires can act as an interfacial layer between bulk silicon and another material grown on top which is not lattice-matched to it.

[00042] Processes of the invention are also applicable to lithium ion battery technology. Silicon has been seen as a desirable candidate for the anode material in lithium ion batteries due to its low discharge potential and high charge capacity. Its application in the past has been limited due to the large change in volume associated with ion insertion and ion extraction. The large amounts of stress and strain that builds in the silicon results in degradation of the silicon layer resulting in a very short performance lifetime. Nanowires have been pursued due to their ability to withstand these stress and strains (see reference (I)). The ability to form well ordered and aligned nanostructures with a great deal of control over the resulting diameter and void spacing between them provided by processes of the invention would be advantageous in making a lithium ion battery anode. In addition, the fact that porous silicon (nanopores or micropores) can also be fabricated via processes of this invention would enable the fabrication of another

anode geometry capable of withstanding the stresses and strains of ion insertion/extraction for lithium ion battery applications.

[00043] It would additionally be possible to form a porous template or silicon nanowire arrays out of a specific type of silicon (say n-type) and utilize an alternate technique like the vapor, liquid, solid (VLS) process to fill the pores with p-type silicon nanowires resulting in a novel n/p junction configuration which could be utilized in a wide variety of optoelectronic (LED, photovoltaic) and electronic (transistor) applications. (For some general information about the VLS process see reference (p).) This process is especially favorable since the Ag particles that catalyze the etching of the silicon substrate to form the template could also be used to catalyze the wire growth (e.g., in VLS or VSS) at the base of the pore to synthesize the wire. In addition, the Ag particles could serve as electrical contacts for the device. A wide variety of materials other than silicon can be formed inside the template as well. A few examples are Bi, Ge, GaN, ZnO, and GaAs.

[00044] Processes of the invention may be used to create nanostructures which make silicon into an intermediate band photovoltaic material (IBPV). (See reference (n).) Silicon has an excellent band structure for IBPV, provided that the strength of particular electronic transitions can be enhanced. One way to do this is to form a dense array of silicon nanowires with specific control over the wire diameter, doping and crystallographic orientation, as described in reference (i). Processes of the invention may be used for manufacturing such nanowire arrays.

[00045] The following references are of interest in relation to this application: (a) K. Peng, Z. Huang, and J. Zhu, *Adv. Mater.* 16 (1) (2004) 73-76; (b) T. Qiu, X. L. Wu, X. Yang, G. S. Huang, and Z. Y. Zhang, *App. Phys. Lett.*, 84 (19) (2004) 3867; (c) H. Fang, Y. Wu, J. Zhao, and J. Zhu, *Nanotechnology* 17 (2006) 3768 and Y. Yang, P. Chu, Z. Wu, S. Pu, T. Hung, K. Huo, G. Qian, W. Zhang, X. Wu, *Appl. Surf. Sci.* 254 (2008) 3061 and X. Li and P. Bohn, *Appl. Phys. Lett.* 11 (16) (2000) 2572 and H. Asoh, F. Arai, S. Ono, *Electrochem. Comm.* 9 (2007) 535; (d) K. Peng, J. Hu, Y. Yan, Y. Wu, H. Fang, Y. Xu, S. Lee, and J. Zhu *Adv. Mat.* 16 (2006) 387; (e) Z. Huang, H. Fang, J. Zhu, *Adv. Fun. Mat.* 19 (2007) pg. 744; (f) K. Peng, M. Zhang, A. Lu, N. Wong, R. Zhang, S. Lee, *App. Phys. Lett.* 90 (2007) 163123; (g) U.S. Provisional Patent Application No. 61/044,573, filed April 14, 2008; (h) U.S. Provisional Patent Application No. 61/195,872, filed October 9, 2008; (i) U.S. Patent Application Publication No. 2007/0278476, filed

February 27, 2007; (j) L. Tsakalakos, J. Balch, J. Fronheiser et al. *App. Phys. Lett.* 91 (23) (2007) 2331-17; (k) M.D. Kelzenberg, D.B. Turner-Evans, B.M. Kayes et al., *Nano Lett.* 8 (2) (2008) 710-714; (l) CK. Chan, H. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R.A. Huggins, and Y. Cui *Nature Nanotech.* 3 (2008) 31-35; (m) U.S. Published Patent Application No. 2007/0190542, filed October 3, 2006; (n) A. Luque, A. Marti, *Phys. Rev. Lett.* 78 (26) (1997) 5014-5017; (o) Q. Shao, A.A. Balandin, *App. Phys. Lett.* 91 (2007) 163503; (p) Y. Cui et al., *App. Phys. Lett.* 78 (2001) 2214-2216.

[00046] All patents, patent applications, and publications mentioned herein are hereby incorporated by reference in their entireties. However, where a patent, patent application, or publication containing express definitions is incorporated by reference, those express definitions should be understood to apply to the incorporated patent, patent application, or publication in which they are found, and not to the remainder of the text of this application, in particular the claims of this application.

Claims

1. An array of aligned silicon nanowires attached to a substrate at a crystalline silicon surface of the substrate, wherein the majority of the nanowires have diameters of no more than about 150 nm and are attached at least approximately perpendicular to the substrate, wherein the crystalline silicon surface at which the array attaches is a crystal plane in an orientation other than (100) and (111).
2. An array as described in claim 1, wherein at least a portion of the silicon surface is coated with silver.
3. An array as described in claim 1, wherein the majority of the nanowires have diameters below the coherence length of electrons or holes in silicon.
4. An array as described in claim 1, wherein the majority of the nanowires have diameters below the de Broglie wavelength of electrons or holes in silicon.
5. An etched nanowire array wherein at least about 75% of the nanowires have a diameter below about 150 nm.
6. The nanowire array of claim 5, wherein the etching is carried out in the presence of an oxidizing agent less reactive than H_2O_2 .
7. A nanowire array comprising polycrystalline silicon.
8. The nanowire array of claim 7, wherein the array is formed by etching a substrate composed primarily of amorphous or polycrystalline silicon.
9. The nanowire array of claim 8, wherein the majority of the nanowires in the array have diameters of no more than 150 nm.
10. A process for etching a silicon-containing substrate to form structures, comprising the steps of:
 - (a) depositing nanoparticles on the surface of a silicon-containing substrate,

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(b) depositing metal on top of the nanoparticles and silicon in such a way that the metal is present and touches silicon where etching is desired and is blocked from touching silicon or not present elsewhere, and

(c) contacting the metallized substrate with an etchant aqueous solution comprising about 2 to about 49 weight percent HF and an oxidizing agent, wherein the process results in nanowire arrays in which the average diameter of the nanowires is less than about 125nm.

11. A process as described in claim 10, wherein the oxidizing agent is oxygen gas bubbled through the etchant aqueous solution.

12. A process as described in claim 10, wherein the metal deposited and patterned in step (b) is silver.

13. A process as described in claim 12, wherein the silver is less than about 50 nm thick.

14. A process as described in claim 10, wherein the result of steps (a)-(c) is a nanowire array where the average nanowire diameter is less than about 100nm.

15. A process as described in claim 14, wherein the result of steps (a)-(c) is a nanowire array where the nanowire diameter is less than about 50nm.

16. A process as described in claim 10, wherein the result of steps (a)-(c) is a tapered nanowire array such that the bases of the nanowires are larger than the tips.

17. A process as described in claim 10, wherein the nanoparticles act as a barrier between the metal and the silicon-containing substrate to prevent the metal from touching the silicon in certain areas of the substrate.

18. A process as described in claim 10, wherein the nanoparticles are used to remove the metal where an etch is not desired and expose the silicon surface.

19. A process as described in claim 10, wherein the silicon-containing substrate prior to deposition of the metal is a bulk silicon wafer.

20. A process as described in claim 10, wherein the silicon-containing substrate prior to deposition of the metal is a silicon-on-insulator wafer.

21. A process as described in claim 10, wherein the silicon-containing substrate prior to deposition of the metal comprises polysilicon or microcrystalline silicon.

22. A process as described in claim 10, wherein the silicon-containing substrate prior to deposition of the metal comprises epitaxially grown silicon.

23. A process as described in claim 10, wherein the silicon-containing substrate prior to deposition of the metal comprises germanium on silicon or germanium on oxide on silicon.

24. A process as described in claim 10, wherein the result of steps (a)-(c) is further processed to produce an optoelectronic device.

25. A process as described in claim 24, wherein the optoelectronic device is a light emitting diode.

26. A process as described in claim 10, wherein the result of steps (a)-(c) is further processed to produce photonic elements and/or waveguides.

27. A process as described in claim 10, wherein the result of steps (a)-(c) is further processed to produce a photovoltaic or solar cell device.

28. A process as described in claim 10, wherein the pattern created by steps (a)-(c) mixes electronic states in the patterned and etched silicon-containing substrate.

29. A process as described in claim 10, wherein the silicon may be chosen to have any desired crystallographic orientation.

30. A process as described in claim 10, further comprising the step of employing the pattern created by steps (a)-(c) as a lithium absorbing component of a lithium ion battery.

31. A process as described in claim 10, wherein the metal deposited in step (b) is continuous such that there are no breaks or cracks that would cause a part of the film to become separated from the remainder.

32. A lithium ion absorbing material comprising silicon nanowires made by metal enhanced etching of silicon.

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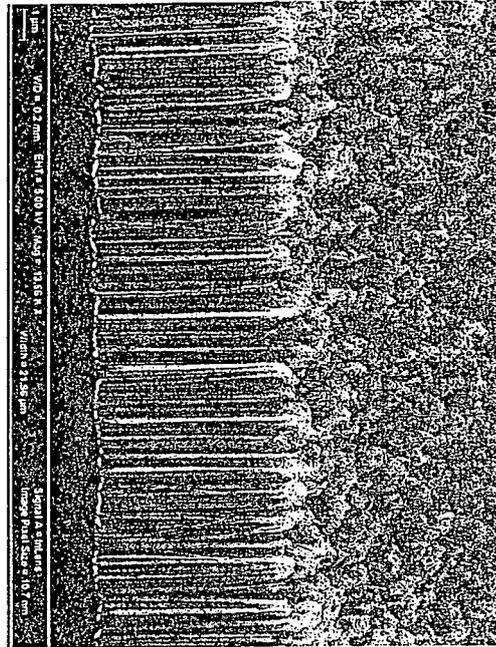
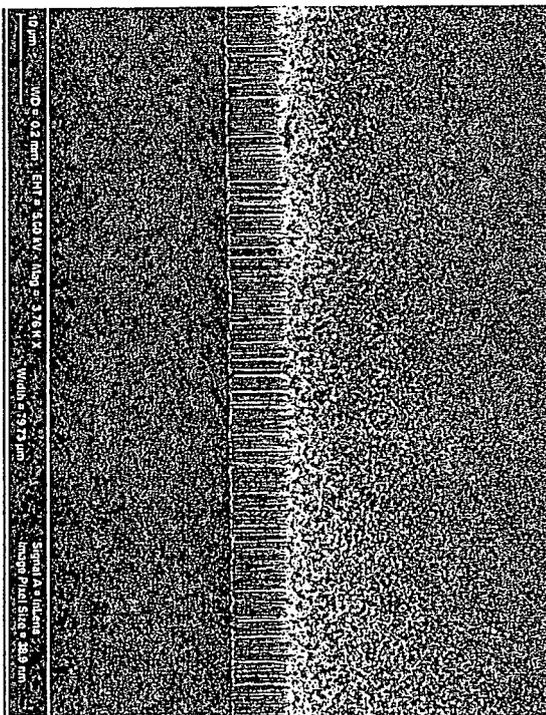


FIG. 1



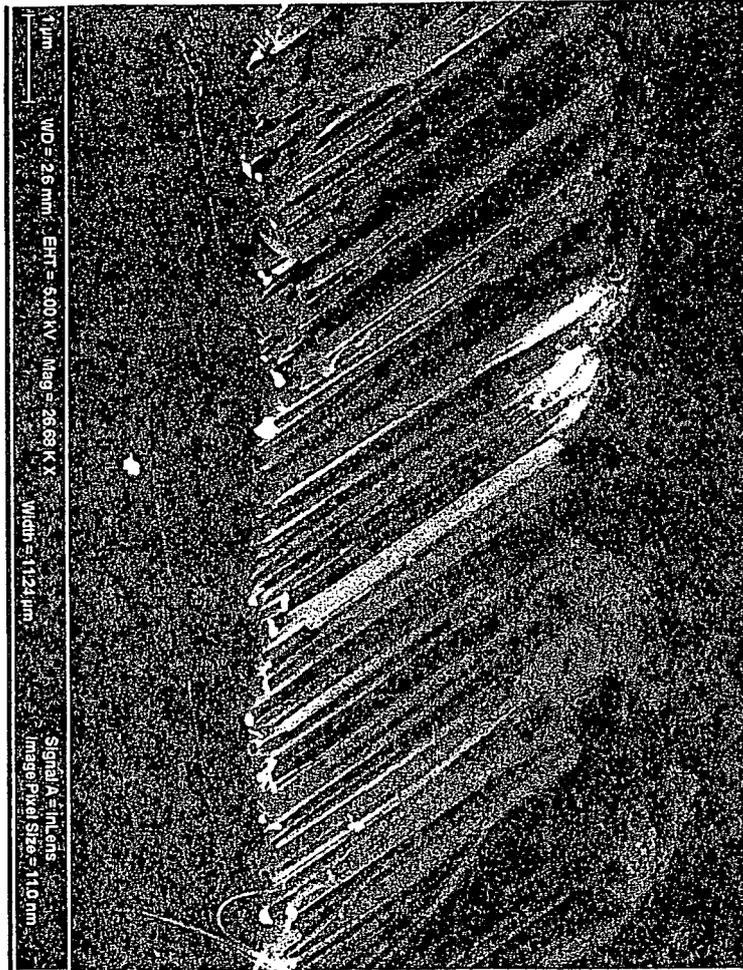


FIG. 2

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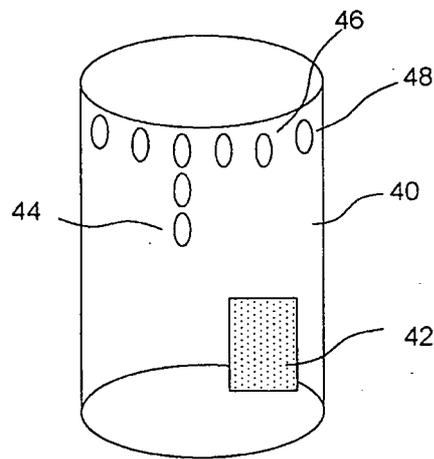


FIG. 3

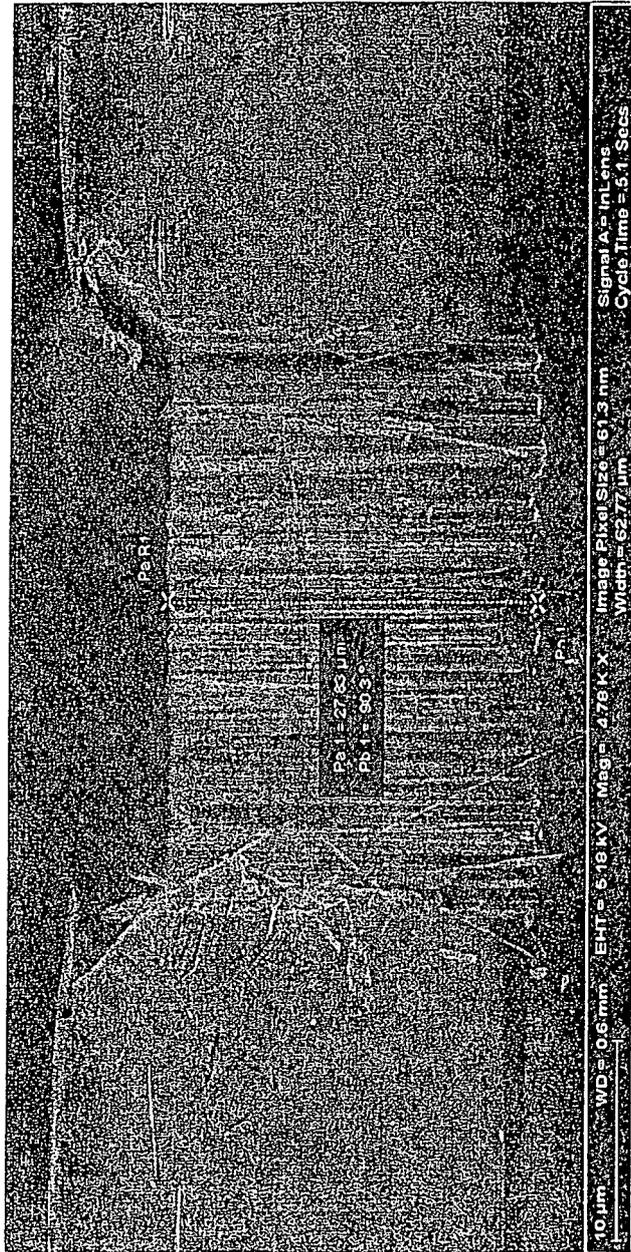


FIG. 4