

New Procedure to Obtain Specific and High Absorbent Silicon Nanotextures: Inverted Pyramids, Cubic Nano-Microholes, Spiroconical Nano-Microholes and Rhombohedral-Stared Nanosheet Bouquets (Nanobuckets)

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Abstract

The present work relates to a process for silicon surface texturing for preparing large-area, silicon nanotextures on silicon substrates at ambient temperature by assisted chemical etching. A novel strategy comprises of two fundamental steps (metal-assisted chemical etching (MACE) and solution post-treatment) of using the silver catalyst to obtain specific nano- or micro-textures. The strategy is based on metal-induced (Ag) local oxidation and dissolution of a silicon substrate in three different concentrations of aqueous fluoride solution with the post-treatment solution. The etching technique is dependent on the etching time and concentration of aqueous fluoride solution. Therefore, detailed scanning electron microscopy observations reveal specific shapes as inverted pyramids, cubic nano-microholes, spiroconical nano-microholes and rhombohedral-stared nanosheet bouquets (called Nanobuckets), obtained for the first time on a (100) silicon surface by this new variant of the MACE method named Double Etching Method (DEM). Silicon nanostructures are used in many nanotechnology applications such as nano-microelectronics, optoelectronics or biomedical applications. UV-Visible spectrometry measurements carried out made it possible to obtain the lowest reflectance and highest absorbance values who are 3% and 97%, respectively for the rhombohedral-stared nanosheet bouquets on (100) crystalline silicon substrates in the UV-visible-NIR wavelength range from 300 to 1200 nm.

Keywords

Silicon Nanotextures, New Procedure, Etching, Reflectance, Absorption

1. Introduction

Black silicon light trapping structures, including nanowires [1] [2] and nano-holes [3] [4], have demonstrated their excellent anti-reflectance properties, providing the opportunities for enhancing light-harvesting. However, despite of the superior light absorption enhancement, the efficiency of textured silicon solar cells remains relatively low compared to those of conventional c-Si solar cells. Therefore, carefully designed new nanostructures such as inverted pyramids (IPs) [5] [6] and nanocones [7] [8] with low surface area enhancement by lithography method, have been done to balance optical gain. Of all these structures, IPs are mostly adopted for its excellent light absorption and the successful fabrication of IPs based solar cells with an efficiency 24.7% further confirms its superiority for high efficiency solar cells [9]. However, the lithography method used for fabricating such structures is costly and time-consuming, which hinders its further implement for mass production. Recently, a cost-effective and efficient approach called metal-assisted chemical etching (MACE) method has been developed to avoid the above disadvantages for industrial mass production. Today, the MACE technique has advanced to a level where desired architectures and surface quality can be readily fabricated; hence, it is becoming one of the main technologies in preparing silicon nanostructures. However, the number of nanostructures or nanotextures shapes is limited with this method and with silver as catalyst. Only nanowires, nanoholes and nanocubes are fabricated using this technique and this catalyst under laboratory applications. To obtain other shapes such as pyramids, inverted pyramids and other morphologies, the addition of post nanostructure rebuilding (post treatment) solution containing additives is needed. In 2014, Ye *et al.* reported an IPs (size of ~ 260 nm) based 156×156 mm² multi-crystalline Si solar cell with an efficiency of 18.45% ($J_{sc} = 36.68$ mA/cm²) by MACE process and a post treatment with low concentration NaOH solution [10]. Until now, two step methods including MACE Black Silicon fabrication and a post structure reshaping process are believed to be a feasible way to connect nanostructure texture with high efficiency Si solar cells [11].

The present work proposes a new method for nanotexturing the surface of a (100) oriented p type silicon substrate in a specific manner with the post-processing solution. More precisely, the new method makes it possible to obtain novel silicon nanotextures shapes for the first time and using only silver as catalyst with any other additive or chemical solution and free external energy at ambient temperature. The new procedure is a variant of the MACE method, called Double Etching Method (DEM) as described in [12].

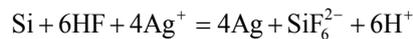
2. Experimental Method

To develop specific micro- or nanostructures an original procedure based on an over-etching of nanotextures allowing to obtain inverted pyramids, cubic nano-microholes, spiroconical nano-microholes and rhombohedral-stared nano-sheets bouquets (nanobuckets), was created. The process is named Double Etching Method (DEM).

A boron doped p-type <100> silicon wafer with a thickness between 600 - 650 μm , with a resistivity of 1 - 5 Ωcm and with a polished surface was purchased from BT Electronics. Before etching, the substrates are degreased and cleaned for 15 min in ultrasonic machine by using acetone, ethanol and de-ionized water solutions, respectively. This step is followed by cleaning with a piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) for 10 min to remove any impurities of organics and rinsed with de-ionized water. Substrates, once rinsed with de-ionized water, are immersed in the etching solution containing HF (4.8, 9.6 and 22.8 M)/ AgNO_3 (0.02 M) mixture in a volume ratio of v: v = 6:19, depending on the desired nanotexture, for a preselected time (30, 60 and 90 min). These concentration ratios, as well as the etching time are varied. The electrochemical reactions involved in this etching step are as follows:



The global reaction is summarized in the following equation:



The samples were placed directly, after rinsing with deionized water, in the HF (40%)/ H_2O_2 solution with a volume ratio of v: v = 20:4 for 30 min. During this step, the nanostructures are created and a nanotextured surface composed mainly of nanowires and nanoholes remains. Their length and depth depend to the first etching time (MACE method). The electrochemical reactions involved are as follows:



The global reaction is summarized in the following equation:



The 3rd step is the innovative and fundamental step responsible for the shapes of the different fabricated nanotextures depending on the pre-nanostructures formed. In this step, the silicon sample thus nanostructured or textured with nanowires, nanoholes, nanopits and/or other nanotextures randomly produced are immersed in a post-treatment solution containing Ag ions for 15 min see **Figure 1**. Then, the Ag nanoparticles deposited are removed by using a concentrated solution of HNO_3 . Surface morphology and chemical composition of the

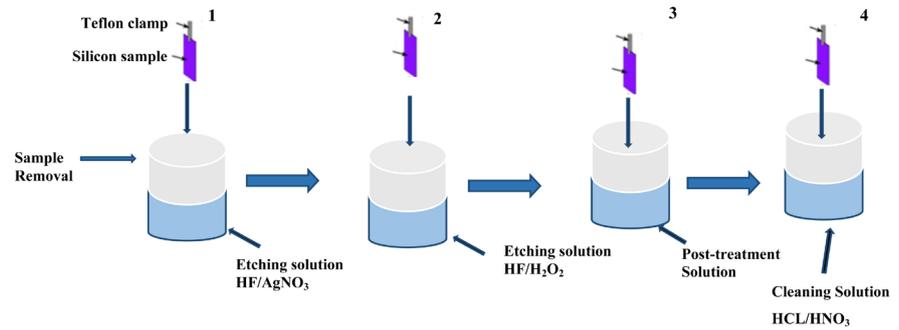


Figure 1. Different basic steps of the double etching method procedure.

Si samples are then characterized by using a MERLIN FEG of Zeiss scanning electron microscopy and energy dispersive X-ray spectrometry (EDX) model in ICMPE (Aix-Marseille-Université), respectively. The total reflectance at normal incidence was measured using a spectrophotometer with an integrating sphere model in LAMBDA 950S integrating sphere in *IM2NP* (Aix-Marseille-Université).

3. Results and Discussions

Figures 2(a)-(d) show SEM images of dispersed inverted pyramids with a 30 min etching time on a (100) oriented p type silicon substrate. The post-treatment with a solution, after the first etching step, made it possible to obtain sparse inverted pyramids (with the catalyst Ag) with sizes varying from 100 to 700 nm approximately (for the HF/AgNO₃ ratio of 4.8/0.02 for 30 min) making it possible to reduce the percentage of reflectance to 10% and thus increasing its absorbance to approximately 90% in the wavelength range between 300 and 1200 nm (**Figure 2(e)** and **Figure 2(f)**). The different obtained inverted pyramids seem to show that the immersion in the post treatment solution is a key step depending on the shape of the initial texture created during the two first steps. Thus for non-symmetrical nanotextures (straits, shallow holes, dots, pits etc.) obtained in those steps with an etching time up to 30 min and a low HF concentration of around 4.8 M, sparse inverted nanopyramids are formed on the silicon surface with a depth varying between 100 and 560 nm.

By increasing the HF concentration from 4.8 to 9.6 M (in HF/AgNO₃ ratio) for the same etching time (30 min), the whole silicon surface is completely covered with dense inverted pyramids (**Figures 3(a)-(d)**). Their sizes varied between 100 nm and more than 2000 nm confirming etchant concentration effects on the holes depth. The change in inverted pyramids density compared to the first ones could be explained by the increase of etching sites on the surface by increasing the HF/AgNO₃ ratio. Optical measurements showed reflection values of less than 10% corresponding to more than 90% absorption in the wavelength range between 300 and 1200 nm (**Figure 3(e)** and **Figure 3(f)**). These values are in agreement with the results from literature for inverted pyramids [13] [14]. The cross-section SEM images of the inverted pyramids structures shown in **Figure 2(d)** and **Figure 3(d)** reveal that the angle between the structured

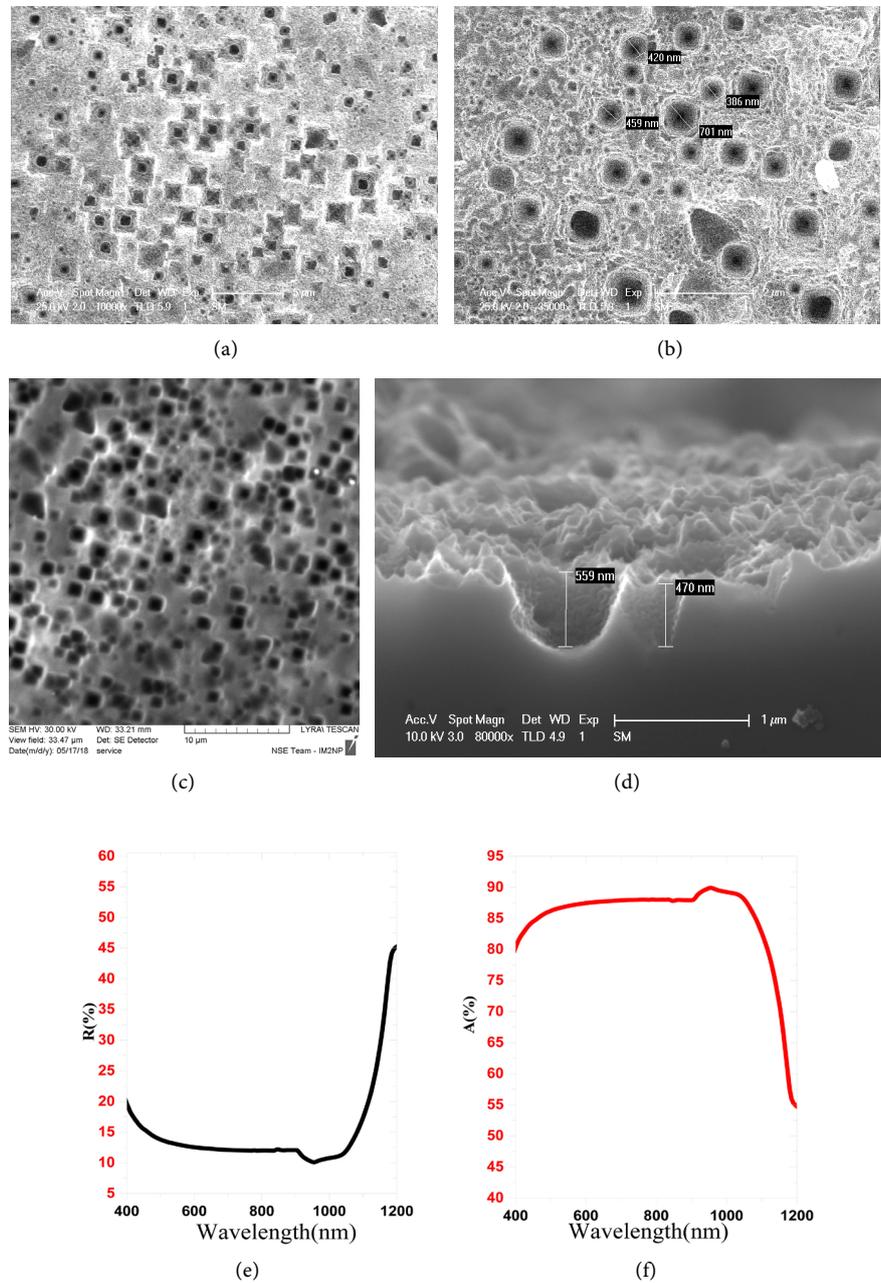


Figure 2. SEM images of sparse inverted pyramids for 30 min etching time in 4.8 M HF concentration (a) front view 10 kX magnetisation, (b) inverted pyramids sizes view, (c) 33.47 μm field view and (d) transverse view and UV-Visible-NIR (e) reflection and (f) absorption for $\langle 100 \rangle$ oriented p type Silicon.

surfaces and the (100) Si surface is around 55° , indicating the Si (111) plane termination of the facets as indicated by [14]. The upper sides of the inverted pyramids show in some cases angle values of more than 120° (polygons, **Figure 3(c)**) indicating the presence of the over etching in this new procedure.

Figure 4 shows SEM images and UV-visible spectra with an HF molar concentration of 4.8 M (in HF/AgNO₃ ratio) for 90 min etching time. Sparse spiro-conical nanoholes with bottom and top diameters between 100 and 400 nm were

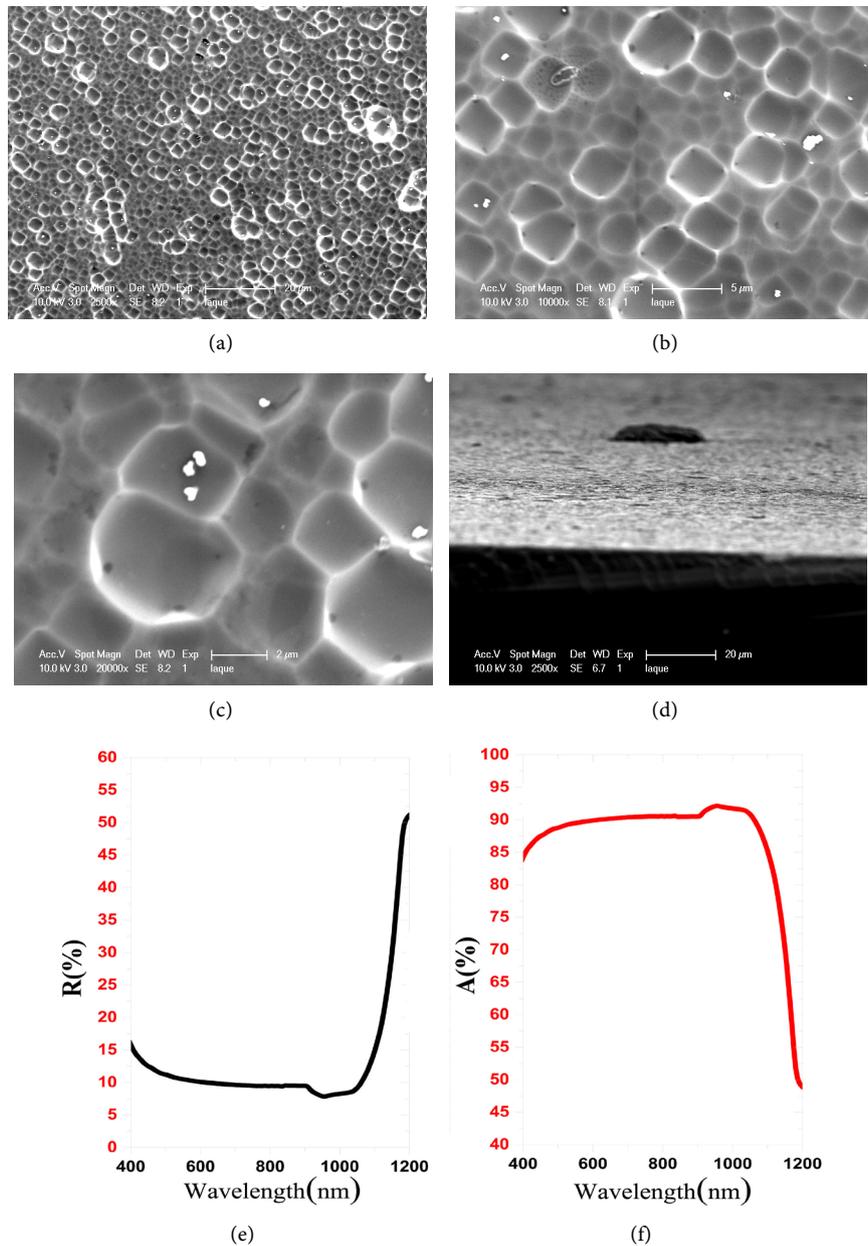


Figure 3. SEM images of p type Silicon with very dense and homogenously distributed inverted pyramids for 30 min etching time and 9.6 M HF (a) front view 2.5 kX magnetisation, (b) 10 kX magnetisation, (c) 20 kX magnetisation, (d) transverse view, UV-Visible (e) % reflexion and (f) % absorption.

obtained. The ratio between top and bottom diameter is around 4. For the second time such specific nanotexture shapes were fabricated in the laboratory of the corresponding authors (the first fabrication has been reported in [12]) (Figures 4(a)-(d)). To obtain such shapes using this new procedure, it needs to be considered that two combined phenomena will take place. One is a physical phenomenon related to fluid mechanics. It is a kinetic mechanism of the movement of a liquid with a high flow rate penetrating a nanohole (vortex movement). The second one is an electrochemical reaction, which takes place in the

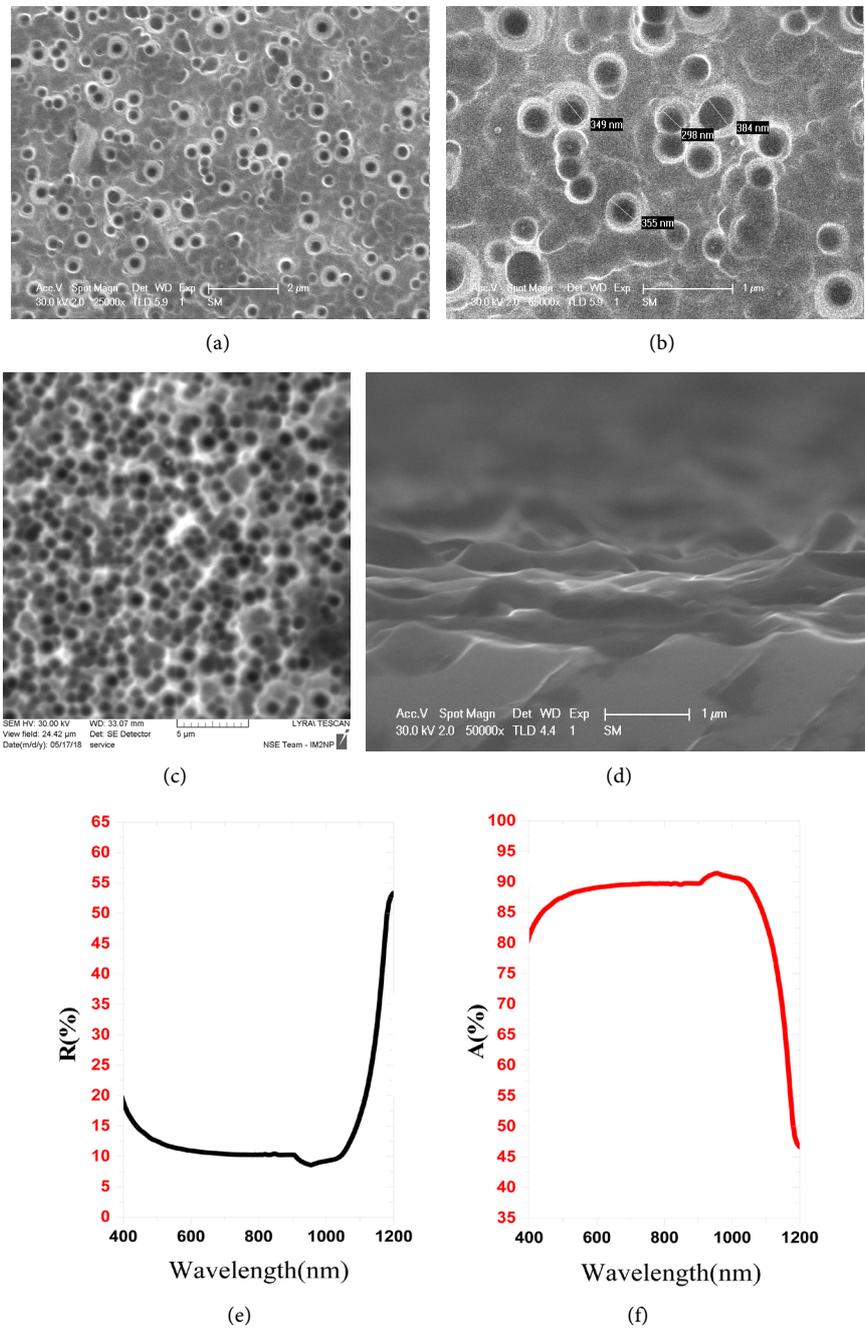


Figure 4. SEM images of p type Silicon spiroconical nanoholes for 90 min etching time and 4.8 M HF (a) front view 25 kX magnetisation, (b) 65 kX magnetisation for nanoholes sizes view, (c) 24.42 μm field view of, (d) transverse view, UV-Visible (e) % reflexion and (f) % absorption.

etching process. The Ag^+ ions will attack the silicon to oxidize it and dissolve it in the solution as detailed in the etching technique due to the presence of the HF/ H_2O_2 solution residues. The use of this solution in the procedure seems fundamental because the presence of H_2O_2 as oxidant at a percentage higher than 30 would increase the horizontal etching speed to the detriment of the vertical etching by annihilating the gravity of the Ag^+ nanoparticles thus preventing it

from descending vertically. The etching phenomenon, linked to the post-treatment solution in a movement mechanism (vortex), result in spiroconical nanoholes (**Figures 4(a)-(d)**). The result can be explained by the relatively long etching time (90 min), permitting to etch more deeply the nanoholes formed in the two first steps of the procedure, compared to the 30 min etching time. This hypothesis is in agreement with the formation of the sparse inverted pyramids, which is explained above, consisting to the formation of straits, pits and pitches (or nanoholes) in the first steps (MACE) and their changing, in the last steps (post treatment solution), to inverted pyramids (**Figure 2**) (or spiroconical nanoholes thanks to nanofluid mechanics (**Figure 4**)). The specific shape of these nanotextures could be used in many applications such as nano- or microfluidic mechanisms in biomedical applications, nanofiltering and nano- or micro-mixing solutions before chemical reactions. These nanostructures gave a reflectance less than 10% and an absorbance more than 90% in the UV-Visible-NIR-range (**Figure 4(e)** and **Figure 4(f)**). FTIR measurement for spiroconical nanostructures gave a transmittance around 1% while the absorption is around 99% between 400 and 4000 cm^{-1} (results not shown here), indicating their interest for IR detectors [15]. On the other hand, the angle between the (100) face of the substrate and the nanocone walls is approximately equal to 54.7° like the one observed in inverted pyramids on (100) Silicon. This indicates that the etching is done along the same axes in addition to the vortex phenomenon.

Increasing an HF molar concentration between 4.8 and 9.6 (in HF/AgNO₃ ratio) makes it possible to obtain a mixture of spiroconical microholes and inverted nanopyramids in interlayers and this for a shorter time of at least 30 min (**Figures 5(a)-(d)**) with reflectance and absorbance values in the UV-visible-NIR of approximately 9% and more than 91%, respectively (**Figure 5(e)** and **Figure 5(f)**). The presence of residual inverted nanopyramids is due to the short etching time (as in **Figure 2**), although the increase in the HF molar concentration has made it possible to obtain a good part of spiroconical nano- and microholes, which are created by the presence of enough deep nanoholes for the vortex movement mechanism. The internal morphology of a selected microhole (**Figure 6(d)**), its uniformity and spiroconical shape, as well as the presence of silver nanoparticles, after etching, confirm the mechanism detailed above. The fabrication of such mixed shapes is in agreement with the hypothesis stated by the authors concerning the role of the pre-etching with help of the MACE method. The surface absorption is comparable to inverted pyramids and spiroconical nanoholes taken individually.

Figure 6 represent SEM images and UV-Visible spectra of cubic micro-holes distributed over the entire surface of (100) oriented p type silicon substrate. Increasing etchant concentration in (HF/AgNO₃ molar ratio from 9.6/0.02 to 22.8/0.02) and the etching time (60 min) makes it possible to obtain cubic microholes which sides varies between 500 and 1000 nm approximately as well as the presence of some residual inverted pyramids (**Figures 6(a)-(d)**). A minimum reflectance and maximum absorbance of around 9% and 91% respectively

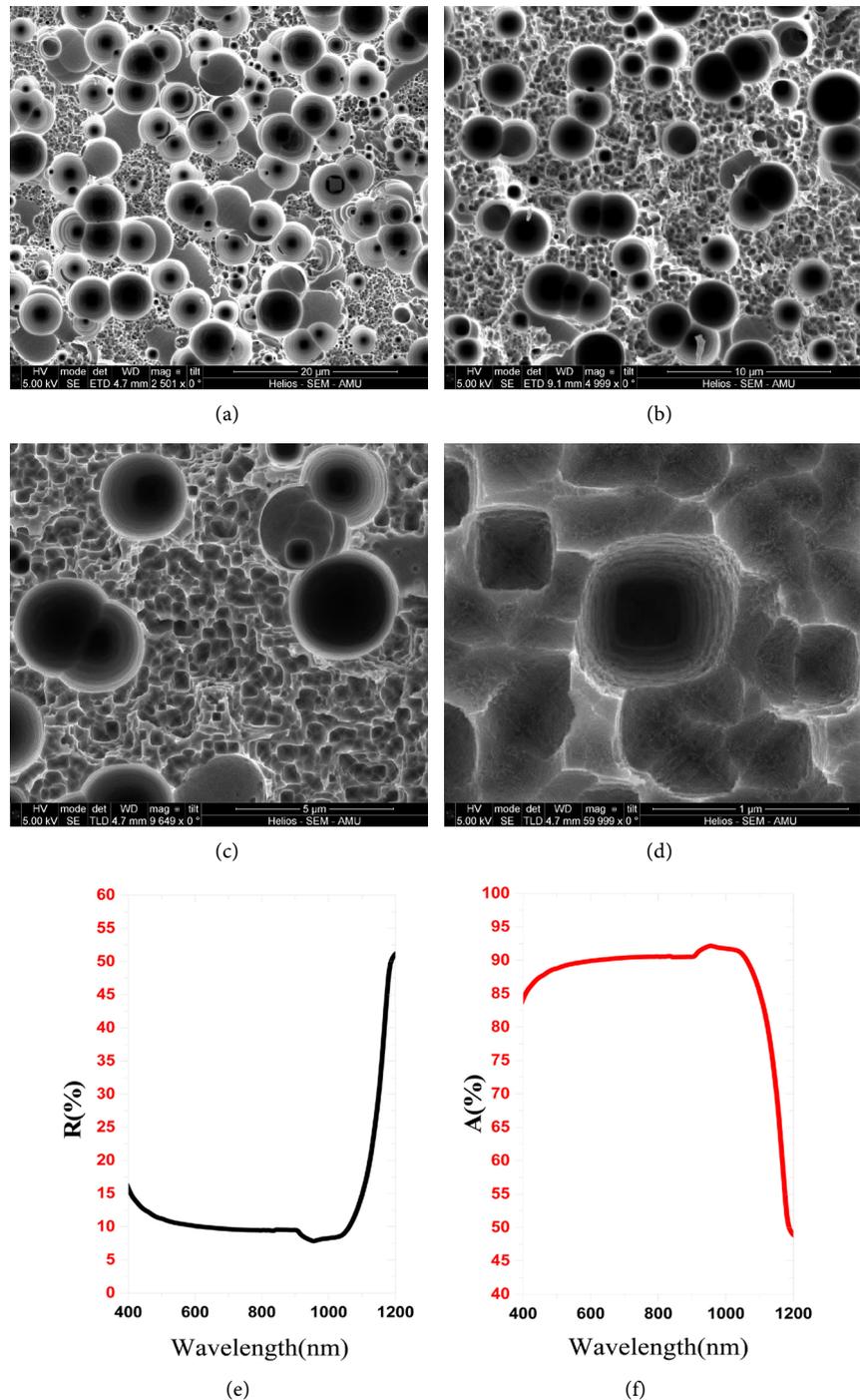


Figure 5. SEM images of p type Silicon mixed spiroconical and inverted pyramids nano/microholes for 30 min etching time and 9.6 M HF (a) front view 2.5 kX magnetisation, (b) 5 kX magnetisation, (c) 9.6 kX magnetisation, (d) 60 kX magnetization and zooming on spiroconical microholes, UV-Visible (e) % reflection and (f) % absorption.

(Figure 6(e) and Figure 6(f)) were obtained. The increase of HF concentration and the etching time permitted to transform the inverted pyramids (Figures 3(a)-(d)) into cubic microholes. The presence of few inverted pyramids confirms this hypothesis.

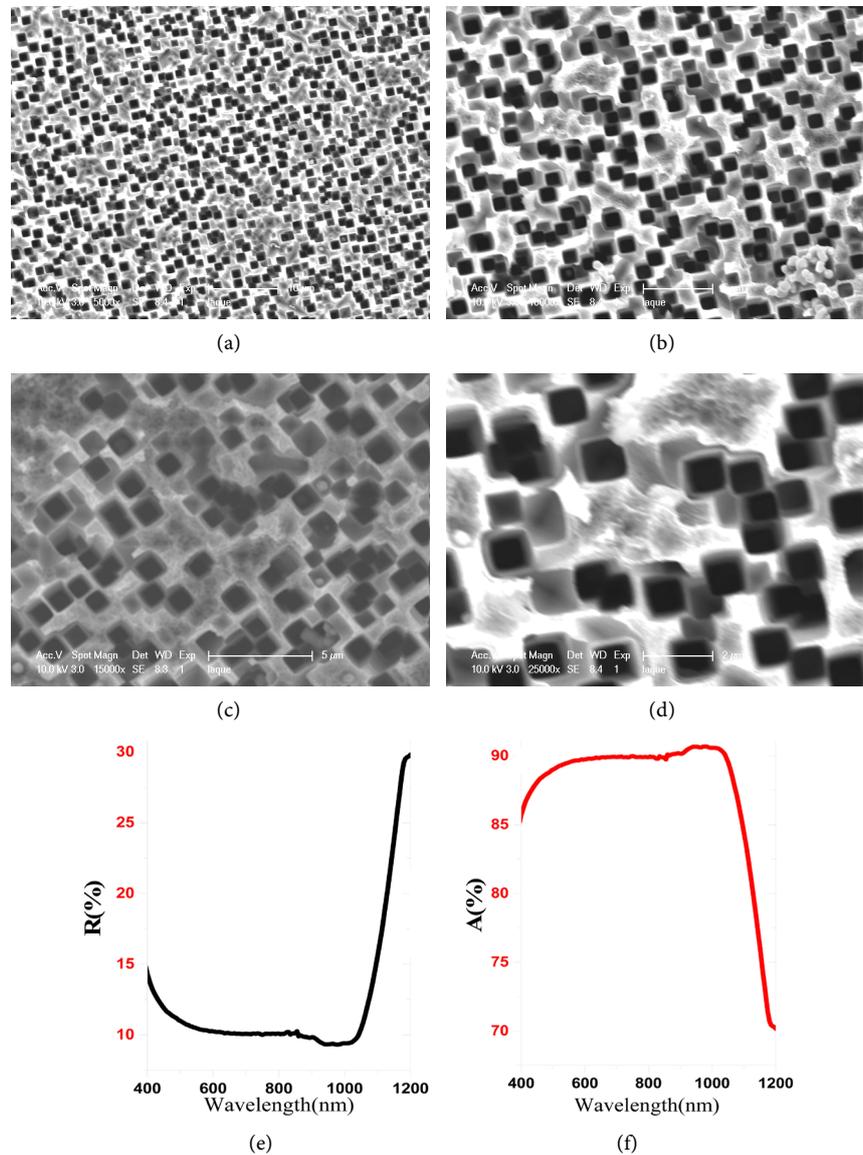
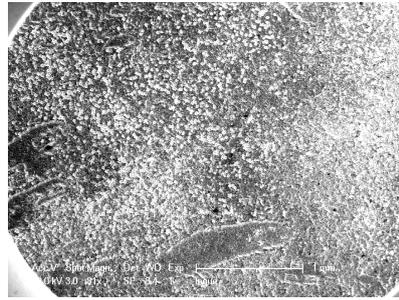
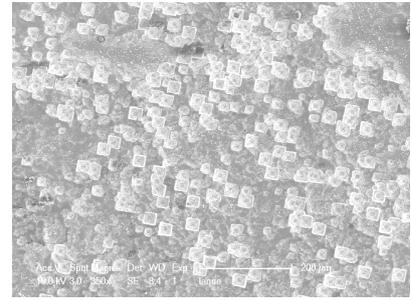


Figure 6. SEM images of $\langle 100 \rangle$ p type silicon cubic nano/microholes for 60 min etching time and 22.8 M HF (a) front view 5 kX magnetisation, (b) 10 kX magnetisation, (c) 15 kX magnetisation, (d) 25 kX magnetisation, UV-Visible (e) % reflection and (f) % absorption.

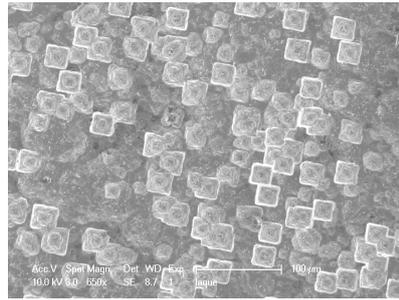
Finally, exceptionally and for the first time, increasing the etching time from 60 to 90 min and with a constant HF concentration (22.8 M), it is possible to obtain specific nanostructures in the form of Rhombohedral Stared Nanosheets Bouquets (Nanoflowers Bouquets named Nanobukets) (Figures 7(a)-(h)). To our knowledge, these rhombohedral superposed silicon nanosheets (Figure 7(g)) are a discovery. They have been fabricated on silicon substrates with a very low reflectance around 3% and a large absorbance of more than 97% in the UV - Visible - NIR wavelength (Figure 7(j) and Figure 7(k)). These results make them one of the best anti-reflective layers for photovoltaic applications. The shape of these nanobukets as well as the morphology of the silicon surface makes



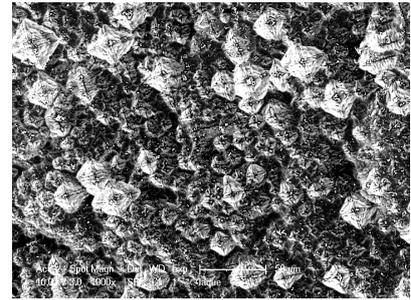
(a)



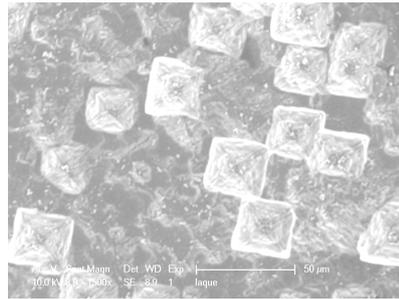
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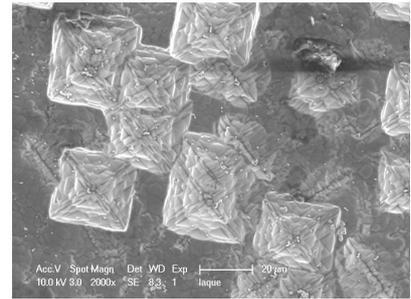
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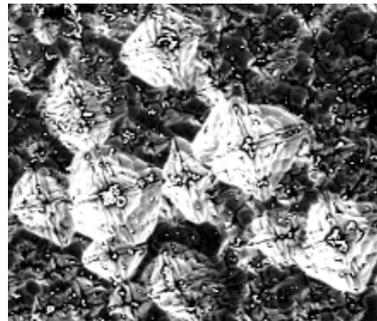
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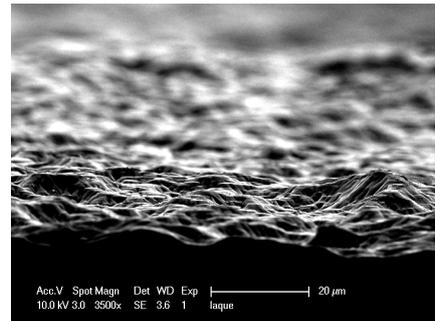
(e)



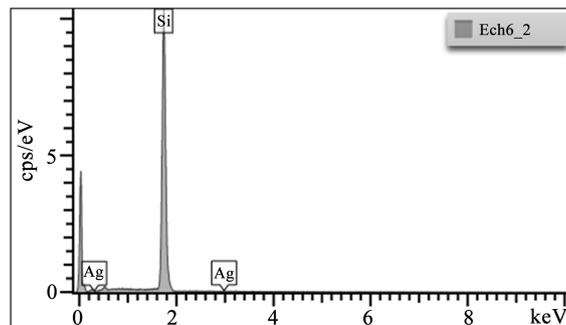
(f)



(g)



(h)



Element	Raie Type	Apparent concentration	k ratio	% Mass	% Mass Sigma	Standard description
Si	Series K	9.00	0.07128	100.00	0.00	SiO ₂
Ag	Series L	0.00	0.00000	0.00	0.00	Ag
Total:				100.00		

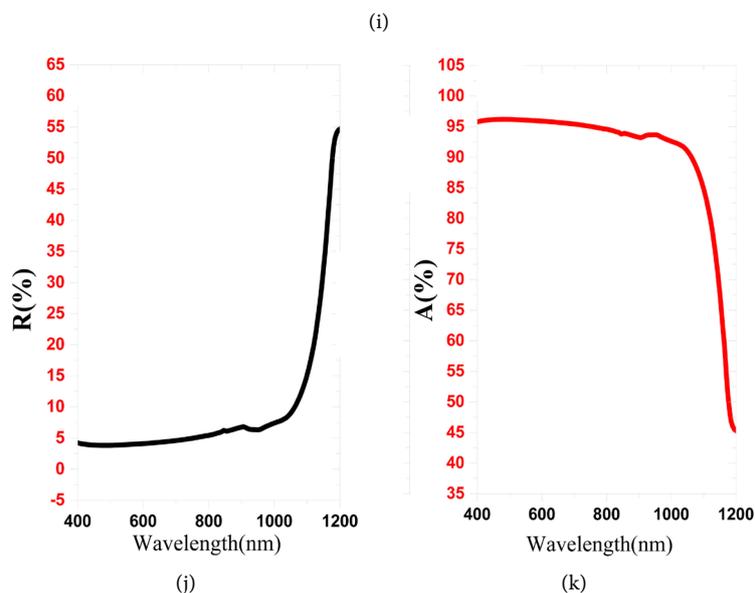


Figure 7. SEM images of $\langle 100 \rangle$ p type silicon rhombohedral-stared nanosheets bouquets for 90 min etching time and 22.8 M HF (a) front view for 0.091 kX magnetisation, (b) 0.350 kX magnetisation, (c) 0.650 kX magnetisation, (d) 1 kX magnetisation, (e) 1.5 kX magnetisation, (f) 2 kX magnetisation, (g) zooming on bouquets for nanosheets view for 1 kX magnetisation, (h) transverse view of the bouquets, (i) EDX spectrum and UV-Visible (j) % reflection, (k) % absorption.

them potential materials for biomedical application. These specific nanosheets can be explained by an over-etching (by increasing the time from 60 to 90 min) of the microholes in preferred $\langle 111 \rangle$ directions thanks to their cubic form thus creating rhombohedral symmetry with axes on the main diagonals of the cube. The etching, done on the (100) faces of the microcubes in an oblique manner, makes it possible to obtain very thin sheets superposed along the C4 axis. The transversal mode shows this thin nanostructure with a quasi-fibrous surface (**Figure 7(h)**) explaining the excellent optical properties. The existence of such nanofibers (**Figure 7(d)** and **Figure 7(g)**) could indicate the growth of another component such as silver nanowires but the EDX analysis (**Figure 7(i)**) permitted to reject this hypothesis showing 100% silicon composition. These results indicate the possibility to obtain silicon nanosheets using such new innovative procedure applicable in industrial level.

4. Conclusion

New and specific silicon nanostructures shapes have been successfully fabricated using a new procedure of metal assisted chemical etching (MACE), using only

Ag as catalyst and post-treatment solution. This variant of the MACE method named Double Etching Method (DEM) permitted to fabricate with the same catalyst:

- Sparse and dense inverted pyramids, which is the second time to have such shapes with Ag catalyst.
- Cubic microholes.
- Spiroconical nano-microholes obtained thanks to the presence of a combination of nanofluidic and electrochemical mechanisms.
- Mixed inverted pyramids and spiroconical nano-/microholes, for the first time.
- And for the first time, exceptional rhombohedral-stared nanosheets bouquets (named here nanobuckets), presenting one of the best optical properties (3% reflection) for silicon nanostructures.

The innovation from this procedure is the possibility to fabricate silicon nanosheets in form of bouquets that opens large possibilities of their use in biomedical and photovoltaic applications. The method is comparable to the nanostructure rebuilding procedure, but no additives are needed in the procedure presented in this work making it very simple and easy.

Acknowledgements

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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