Silicon Nanowires Synthesis by MACE

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Silicon is the undisputed leader for microelectronics among all the industrial materials and Si nanostructures flourish as natural candidates for tomorrow's technologies due to the rising of novel physical properties at the nanoscale. In particular, silicon nanowires (Si NWs) are emerging as a promising resource in different fields such as electronics, photovoltaic, photonics, and sensing. Despite the plethora of techniques available for the synthesis of Si NWs, metal-assisted chemical etching (MACE) is today a cutting-edge technology for cost-effective Si nanomaterial fabrication already adopted in several research labs. During these years, MACE demonstrates interesting results for Si NW fabrication outstanding other methods. A critical study of all the main MACE routes for Si NWs is here presented, providing the comparison among all the advantages and drawbacks for different MACE approaches. All these fabrication techniques are investigated in terms of equipment, cost, complexity of the process, repeatability, also analyzing the possibility of a commercial transfer of these technologies for microelectronics, and which one may be preferred as industrial approach.

Keywords: silicon ; silicon nanowires ; MACE metal-assisted chemical etching ; nanotechnology ; CMOS-compatible

1. Introduction

In the last half-century, microelectronics and telecommunications have completely changed our world. The two application fields have in common the use of silicon (and silicon oxide) technology for both integrated circuits and optical fibers. The huge abundance on earth combined with its low-cost and its good electrical properties made the Si extremely advantageous compared to other semiconductors. Moreover, the stability, the easy and finely controlled realization of silicon oxide have determined the arising of Si as the leading material of the current technology, even outstanding germanium. Since 1970, we saw the doubling of Si transistors inside the same integrated circuit area approximately every 2 years. This technological trend was discovered by Moore, and is known as Moore's law ^{[1][2][3]}. However, the trend has started to change in the last decades, reaching the saturation regime due to the complexity of a further down-scaling.

Nowadays, one of the strictest limits is represented by the interconnection bottleneck. The dimension decrease implies longer and so, more power- and time-consuming interconnections, in addition to a more complex circuit realization ^[4]. The interconnection bottleneck due to RC delays limits the advantages of device downsizing, hindering their further downscaling. These issues are not the concern of a future challenge but are already present today.

The arising of new physical phenomena on the nanoscale promoted the emerging of Si nanostructures for the past, present and future technologies. In particular, silicon nanowires (Si NWs) developed as a novel resource in many different fields, such as electronics ^{[5][6][Z]}, photovoltaics ^{[8][9][10]}, photonics ^{[11][12][13]}, and sensing ^{[14][15][16]}, as schematized in Figure 1.



Figure 1. Schematic showing the main application fields of silicon nanowire from the top corner to the left one in clockwise order: Electronics with a Si NW Field-Effect Transistor ^[2], Sensing with a Si NWs-based gas sensor ^[16], Photonics with Si NW luminescence ^[11], Energy with a solar cell based on a vertically-aligned Si NWs array ^[8]. Top ^[7] and right ^[16] images are reproduced with permission, Copyright 2005 and 2011, IOP Publishing. Bottom ^[11] and left ^[8] images are reproduced with permission, Copyright 2010, American Chemical Society.

Indeed, 1D nanostructures can be easily integrated in the typical flat architectures of integrated circuits, benefitting from such nanomaterials' advantages.

During these years, a lot of effort was spent on the realization of novel Field Effect Transistor (FET) based on Si NWs ^[12] ^{[18][19]}, as well as on the integration of silicon photonics in microelectronics industries ^{[11][20][21]}. Metal Oxide Semiconductors Field Effect Transistor (MOSFET) technology's constant miniaturization for microelectronics led scientists to design new improvements based on nanomaterials, such as nanowires and nanotubes. Si NWs arise as a natural candidate, and Lieber's group ^[5] showed their substantial advantages on the state-of-the-art of planar silicon FET transistors. Their Si NW FET was obtained using the same planar geometry on a silicon bridge between the source and the drain. The FET was realized with p-type Si NWs having diameters of 10–20 nm dispersed on a 600 nm silicon oxide layer on top of a silicon wafer. Moreover, the paper of Feng et al. ^[6] reports a low-frequency noise behavior of Si NW FET compared to the planar standard due to the electrons quantum confinement in 1D. As an example of a typical Si NW FET architecture, the device obtained from Koo et al. ^[7] is shown at the top of <u>Figure 1</u>.

2. Silver Salt and Single Step MACE

In 2002 Peng et al. realized a high density of vertically aligned Si NWs with the MACE by using an AgNO₃:HF aqueous solution in a teflon-lined stainless-steel autoclave ^[22]. After three cleaning steps in acetone, ethanol, and diluted aqueous HF solution to remove organic grease and native oxide, the cleaned wafer was etched with 5.0:0.02 M solution of HF:AgNO₃ and treated at 50 °C for 60 min. During the etching process, the silicon wafers showed the formation of a thick layer of Ag dendrites on top of the nanowires, which is promptly removed by nitric acid solution (70%). Indeed, due to the formation of silver precipitates and to the use of AgNO₃, this method is commonly known as the silver salts approach and it is identified as the main single step MACE approach.

In <u>Figure 5</u>a–d the scheme of the silver salt process is shown in detail. After the cleaning procedure, the sample is immersed in an aqueous $AgNO_3$:HF solution (<u>Figure 5</u>a). When in solution, the $AgNO_3$ catalyst precipitates forming Ag nanoparticles (NPs) which are randomly distributed onto the silicon flat surface, catalyzing the HF driven Si etching in a very similar way to the one described for H_2O_2 . Indeed, $AgNO_3$ acts both as an oxidant and as a metal source. Ag NPs, with dimensions and density related to the starting silver nitrate solution, precipitate onto the Si surface biasing the etching. The Ag nanoparticles formed in solution are more electronegative than the Si and inject holes into the substrate that is oxidized due to the presence of radical NO_3^- . The selective oxidation process is driven at the Ag NPs/Si interface resulting in the formation of SiO₂ underneath the metal NPs, and the etching continues by the HF presence, resulting in the formation of Si nanowires in the Si uncovered regions. As a byproduct of the process, Ag dendrites are formed onto

the newly etched Si NWs as depicted in the scheme in <u>Figure 5</u>b. The Ag dendrites form a dense network of several microns thick (about 40 μ m) onto the Si NWs, as displayed in the SEM cross-section (<u>Figure 5</u>d). Finally, the silver dendrites in excess are selectively etched by nitric acid (<u>Figure 5</u>c) and the Si NWs vertical array are obtained as shown from the SEM cross-section (<u>Figure 5</u>e).



Figure 5. Scheme of Si NWs synthesis by silver salt single step MACE: (**a**) Ag precipitation from the HF/AgNO3 solution onto the Si surface, (**b**) Ag dendrites and Si NW formation, (**c**) Ag dendrites removal by nitric acid. Cross-section SEM of Si NW realized onto p-type (111) by HF/AgNO₃ single step MACE for 30 min, (**d**) during Ag dendrites formation, and (**e**) after its removal ^[23]. (**f**) SEM plan view of Si NWs produced by HF/KAuCl₄ synthesis after 30 s ^[24]. (**d**,**e**) ref. ^[23] are reproduced with permission, Copyright 2006, John Wiley and Sons. (**f**) ref. ^[24] is reproduced with permission, Copyright 2005, John Wiley and Sons.

<u>Figure 5</u>e shows the typical cross-section of Si NWs realized by using a HF/AgNO₃ solution for 30 min with concentrations of 4.6/0.02 M. The Si NWs were obtained onto a (111) p-Si substrate preserving their crystalline quality, and are about 4 μ m long ^[23]. The average diameter of NWs realized by single step approaches is about 70 nm ± 20 nm ^[25] as usually obtained by the silver salt approach, ranging from about 60 nm up to 140 nm on average ^[26]. As already stated, the length of the NW array can be increased with the etching time from a few hundreds of nm up to several tens of microns, leading to nanostructures with an aspect ratio above 200 ^[27]. Aside from AgNO₃ precursors, also KAuCl₄ is widely diffused for the single step MACE process. The SEM plan-view of Si NWs obtained by MACE with HF/KAuCl₄ with concentrations ratio of 6.0/0.005 M after 30s, as shown in Figure 5f ^[24].

This single step silver salts MACE process is fast, does not need complicated sample preparation, and is less expensive than the other MACE procedures. In their pioneering works, Peng et al. investigated the strong correlation of the growth parameters, mainly the solution type and concentration, growth temperature, illumination, and substrate orientation.

Indeed, a variety of oxidative metal-based solutions can be used to drive the Si etching, such as $AgNO_3$ ^{[28][29]}, $KAuCl_4$ ^[24], $Fe(NO_3)_3$ ^[30], $KMnO_4$ ^[31], $KBrO_3$ ^[32], $K2Cr_2O_7$ ^[31], and so on, however Ag and Fe-based oxidants presents the lowest redox potential ^[33]. Additionally, different noble metals such as Ag, Pt, Fe, Pd, and Au are mainly used to catalytically reduce H_2O and O_2 ^{[34][35][36]}. In general, dendrite structures are produced during the oxidation and dissolution of the Si substrate when the metal ions are reduced to particles, resulting in the formation of vertically aligned Si NWs with differences in the oxidation and etching rate, and for the NW morphology ^[33]. Higher concentrations of the metal salts result in a denser metal catalyst, hence forming nanowires with lower density, smaller diameter, and more spaced within each other. Indeed, it is not simple to control the NW planar arrangement by this approach, since their diameter, density, and interspacing are determined by the metal concentration.

Another parameter highly affecting the morphologies of the etched NWs is the type of noble metal used during the MACE. Usually, Ag and Au nanoparticles formed in solution result in straight pores during the etching, while straight or helical pores can be achieved by Pt catalyst were reported by Tsujino et al. ^{[37][38]}. Indeed, through its precipitation, Pt nanoparticles move randomly during the etching, resulting in curvy pores without a uniform etching direction. Moreover, the formation of porous nanostructures is also influenced by metal. Generally, Au-coated or Ag-coated substrates result in smoother NWs with low porosity, while Pt-driven synthesis results in a more porous structure ^[37]. Similarly, while standard

p and n doping results in a similar etching rate for the formation of low porosity NWs, the presence of a high concentration of dopants (around 10^{20} dopant atoms × cm⁻³) for p++ and n++ Si wafers results in the formation of highly porous Si NWs due to the occurrence of lateral etching.

Peng's MACE synthesis is a single step approach for the easy and fast formation of Si nanowires without the need of a second etching step in other oxidizing species such as H_2O_2 ^[39] or thin film depositions ^[40].

In general, this process is carried out at room temperature although the correlation between the temperature and the etching rate structure was also studied. The NW length approximately follows a linear trend with time. However, the etching rate also depends on the temperature and increases linearly between 0° to 50 °C ^[41]. Another parameter affecting the etching rate is illumination. If the intensity of illumination is sufficiently high so that the injection of the photoexcited holes is comparable or higher than the concentration of holes injected from the oxidant species, then the etching occurs faster. Studies revealed that the process is independent of the room illumination within a confidence of 5%, but an increment of about 1.5 times the etching rate was observed under light illumination with a 20 W lamp ^[42].

To control the axial orientation of vertically aligned Si nanowires it is possible to vary the Si wafers with other orientations, such as (100) and (110). According to the back-bond breaking theory $^{[43][44]}$, the (100)-orientation presents the lowest bond energy and so (100) wafer are preferentially etched vertically along with this orientation. In contrast, an atom on the (110) and (111) have three back-bond to break, hence the etching occurs again preferentially along the (100) when the etching rate dominates on the oxidation process. On the contrary, increasing the oxidant concentration favors the etching of non-(100) orientation resulting in tilted nanowires $^{[45][46][47]}$.

However, a crucial drawback compared to the other MACE approaches is that during the process the presence of Ag dendrites is attested onto the samples and the dendrites etching may damage the Si NWs, resulting also in Ag contaminants ^[48]. Hence, the MACE single step methods allow to achieve high yield, fast production rate at the expense of a lack of control on the NWs planar arrangement and diameter control ^[23].

Indeed, more advanced syntheses were optimized by using masked approaches, granting also the control on the NWs diameter and planar arrangement (density and spacing) by using single-step MACE coupled with lithography processes.

As an example, Nassiopoulou et al. used UV photolithography onto p-type (100) Si wafers with resistivity ranging of about 1 Ω × cm to open square-shaped windows ranging from 2 × 2 μ m² to 400 × 400 μ m² with the AZ5214 photoresist applied by spin coating, as shown in <u>Figure 6</u>a,b. Then, Si NWs were grown by MACE in a AgNO₃/HF/H₂O solution with a concentration ratio of 0.67 g:35 mL:182 mL at a temperature of 30 °C, as reported in <u>Figure 6</u>c. <u>Figure 6</u>d shows the top-view SEM microscopies imaged of the exposed windows where Si NWs are grown, confirming the efficiency of this approach. The SEM cross-section reported in <u>Figure 6</u>e,f shows that it is possible to grown 15 µm long vertically aligned Si NWs with good quality even at the window edge, confirming the robustness of two-steps MACE methods. Nonetheless, photolithography is limited to small areas of about 10⁴ µm² ^[49], and other approaches based on two step MACE using films achieved by the metal deposition onto silica bead can also be used ^[50].



Figure 6. Flow chart for Si NW formation by MACE at a temperature of 30 °C on the confined areas by (**a**) applying AZ5214 photoresist, (**b**) opening windows from $2 \times 2 \mu m^2$ to 400 \times 400 μm^2 , and using (**c**) AgNO₃/HF/H₂O solution with a concentration ratio of 0.67 g:35 mL:182 mL. (**d**) Plan-view and (**e**,**f**) Cross-sections SEM images of the etched confined areas ^[49]. This figure ^[49] is reproduced with permission (open access), Copyright 2011, Springer Nature.

The primary catalysts for MACE are Ag, Au, and Pt because of their stability and catalytic activity in HF/ H_2O_2 solution, but apart from their high cost, the main drawbacks of these noble metals are their diffusivity in Si, which is detrimental to the performance of CMOS ^[51]. As an alternative W and Ni can also be used. Both W/ H_2O_2 and Ni/ H_2O_2 result in a lower etching rate compared to noble metal, the first one allowing the production of very large holes up to 800 nm in diameter and the latter resulting in the formation of pyramidal etched structures ^[52].

Gallium and Platinum ions deposited by focused ion beam can also be adopted for the Si MACE ^[53] and the produced NWs show poor morphology and low reproducibility.

Ti metal was also introduced to HF/ H_2O_2 aqueous etchant to etch Ag-loaded Si (n-type, 100) ^[54], resulting in a lower etching rate by increasing Ti concentration. This decrease was attributed to the lowering of H_2O_2 concentration because TiF_6^{2-} produced by the reaction of Ti and HF can complex with H_2O_2 to form anions of $[TiF_6(H_2O_2)]^{2-}$.

Similar to AgNO₃, also AgO (insoluble) ^[55] and Ag₂O (soluble) ^[56] have been utilized instead of AgNO₃ in one-step MACE always forming Ag dendrites as a byproduct. The activation energy of Si etching for HF/AgO and HF/Ag₂O are lower smaller than HF/AgNO₃, being 0.20 eV in HF/AgO etchant ^[55], and 0.15 eV in HF/Ag₂O etchant ^[56].

The same MACE techniques used for Si NWs synthesis can also be used for the production of Si microstructures ^[57], and 3D structures ^[58].

Si microstructures are easily obtained in a sequence of steps that include selective MACE Si NWs in pre-patterned regions by masked photolithography, which are then sacrificed in an over-etching process leaving the microstructures standing. Si microstructures first synthesis step consists of the patterning realization on Si wafer by photolithography, deposition of noble metal catalyst for MACE in HF/oxidants solution to produce Si nanowires only in the patterned areas, and then etching away the Si nanowires in a KOH-based solution ^[59]. To allow the MACE processing, noble metal (mainly Ag, Au, and Pt) can be deposited onto the Si surface by different methods which include thermal evaporation ^{[60][61]}, sputtering ^[47], electron beam evaporation ^[27], electroless deposition ^[24] and spin coating ^[62]. The whole process can be carried out at room temperature without complex equipment or special facilities, and it can be applicable on a wafer-scale.

3. Metal Film or Two Step MACE

In the literature it is possible to find both the name of *metal film* and *thin film* approaches for several types of two step MACE routes. In this paragraph will be presented all the methods reporting the use of metal film in the literature.

Metal film can be deposited on Si wafer and used as a metal catalyst in a MACE approach. Several works report the use of metal film to offer several advantages in terms of geometry control, diameter, spacing, and density ^{[27][47][61][63][64]} compared to MACE approaches that involve layers of nanoparticles similarly to single step MACE (e.g., the silver salts). The metal geometry determines the formation of silicon nanostructures and self-assembly methods can also be used for masking. Most of the approaches take advantage of metal films integration with some masking methods to strictly determine the geometry of the metal array (negative mask of the silicon nanowire array). Indeed, to surpass the lack of control in the Si NWs array geometry, the MACE can be coupled with self-assembly or a lithography process by using ordered metal film as catalysts. This method can be used to realize several silicon nano- and microstructures with a very high aspect ratio, surpassing the limit of 50:1 typical of DRIE. Different groups ^{[65][51]} report the use of MACE by high control patterned metal films (usually obtained through EBL) for nano and microfabrication of silicon. This approach can be used to fabricate Si gratings ^[65], honeycomb array ^[66] and other microstructures ^{[67][68]} or vertical aligned ^{[33][51][63][69]}, tilted ^{[46][70][71][72]}, zigzag ^{[73][74][75]}, or tapered Si nanowires ^[76].

A typical approach is the one of Miao et al. $[\underline{66}]$ used to realize a silicon honeycomb array. This array was obtained by depositing the metal in a previously patterned resist, in this case, exposed and developed by UV lithography. After the lift-off, the metal results structured as the negative of the resist mask. After a typical MACE process at room temperature in a HF/H₂O₂ bath (H₂O₂ 30 wt.%, HF 40wt.%), they obtained a honeycomb array of 50 µm width and 280 µm deep $[\underline{66}]$.

Another possible approach reported by Li et al. ^[65] consists of patterning the metal (Ti-Au) through an RIE process. Initially, a 3 nm of Ti as an adhesion layer and 20 nm of Au is deposited by EBE in a Si substrate. The sample is then spun with PMMA and patterned through EBL. The pattern realized through EBL corresponds to the final structure. In fact, the exposed metal is then etched by RIE and then the PMMA is removed. Finally, the sample is immersed in a H_2O_2 :HF solution with the hydrogen peroxide used as an oxidation agent and a high aspect ratio is obtained with Si structures characterized by a length of 250 nm and a height of 21 μ m.

Yeom et al. report the use of nanosphere lithography for the fabrication of Si NWs through MACE as visible in Figure 7. [77]. In particular, in Figure 7 at the schematic of the nanosphere lithography for the realization of the Ti/Au metal film used as a catalyst is shown. After the reduction of the nanosphere dimension by RIE a Ti adhesion layer of a few nm was deposited and then followed by 10–25 nm of Au deposition. In Figure 7b–d, the main possible issues related to the nanosphere etching by RIE are reported. Figure 7b shows that a continuous RIE reduction can increase the roughness of the nanospheres or it can ruin the starting spherical shape (Figure 7c). Another issue is the formation of a continuous

metal film (<u>Figure 7</u>d) that completely covers the nanosphere, making the lift-off process very difficult. Finally, in <u>Figure 7</u>e the authors show that as a function of the etching solution main parameters is possible to obtain tapered and porous Si NWs.



Figure 7. (**a**) Scheme of the Si NWs fabrication by nanosphere lithography coupled with MACE. In particular: (A) nanosphere reduction, (B) lift-off process, and (C) metal-assisted chemical etching. SEM images of the main issues and challenging steps of the process: (**b**) roughened nanosphere due to the RIE etching, in the inset a single roughened nanosphere is shown with a scale bar of 100 nm; (**c**) nanosphere shape ruined after excessive RIE, (**d**) unsuccessfully lift-off of an Au layer, (**e**) tapered and porous Si NWs by MACE ^[77]. This figure ^[77] is reproduced with permission, Copyright 2013, John Wiley and Sons.

Several types of masking procedures are being used during these years besides the elicited EBL. Wendisch et al. report on the use of colloidal lithography followed by a plasma treatment to reduce the nanosphere size ^[78]. Kim et al. ^[63] demonstrate the use of an anodic aluminium oxide mask also used in several other works ^{[79][80]}. Other types of diffused masking procedures are polystyrene spheres ^[61], laser interference lithography ^[81], superionic solid state stamping ^[70], and block copolymer lithography ^{[22][82]}, and even Focused-Ion Beam (FIB) ^[53].

Despite masked approaches permits to achieve a high control on the Si structure geometry, quantum confined Si NWs remain very complicated to be obtained due to the required resolution of few nanometers. Different authors ^[12] demonstrate the application of MACE without masking approaches. To surpass the common diameter limitations, the group of Irrera engineered a metal film approach by using few nanometers of Au or Ag discontinuous layers. By the percolative self-assembly of the gold obtained at the right deposition condition, this method permits to obtain Si NWs with an average diameter of few nanometers and with a very high density. In this case, no masking procedures are applied and the NWs geometry is determined by the negative development of the percolative gold geometry.

As shown in Figure 8a–d, a discontinuous thin metal film is deposited by EBE on an oxide-free Si substrate (Figure 8a,b). The sample is then immersed into a watery solution of H_2O_2 :HF (around 0.44 M:5 M) with the metal that drives the Si oxidation and so the etching by the HF (Figure 8c). Silicon nanowires are realized on the uncovered region, and the gold is finally removed by a gold etchant solution (Figure 8d). All the processes are performed at room temperature. The presence of the gold is not attested inside the Si NWs by using Energy Dispersive X-ray analysis and Rutherford Backscattering Spectrometry [83][84].



Figure 8. Scheme of Si NW synthesis by thin film MACE: (**a**) native oxide etching, (**b**) thin metal film deposition by EBE, (**c**) metal-assisted chemical etching, (**d**) gold etching. All the processes are performed at room temperature. (**e**) Cross-section SEM images showing the possibility to tune the NW lengths from hundreds of nanometers to several micrometers. (**f**) Tilted Cross-section SEM showing the high NW density of about 10¹² NWs/cm². Raman analysis of the first order stokes silicon peak. The average Si NW diameter is obtained for each different metal by fitting the Raman peak with the Campbell-Fauchet model ^[85]. (**g**) Normalized PL spectra of the different NW samples.

As shown in <u>Figure 8</u>e, by changing the etching time the Si NW length varies from a few hundreds of nanometers to several micrometers. Therefore, as visible in <u>Figure 8</u>f the density of the Si NWs is huge (about 10¹² NWs/cm²) and this is a crucial point for all the applications. NW walls are smooth and with high crystalline quality, as previously observed by TEM ^[84]. The average diameter of these synthesized Si NWs is determined by the thickness and the type of metal used as a catalyst. In fact, the thin metal layer is discontinuous and nanometric areas of uncovered silicon are present. The average dimension of these areas is determined by the material wettability and thickness. By using 10 nm of Ag, 2 nm of Au, and 3 nm of Au an average uncovered Si diameter of 12 nm, 9 nm, and 7 nm, was respectively demonstrated. These data were obtained from the statistical analysis performed on the SEM characterizations of the different films. The dimension of the diameters of these uncovered Si holes is strictly related to the final Si NW average diameters.

In particular, for the different metal thin films, the Si NW average diameters were obtained through Raman analyses. Indeed, the Raman signals of the Si are asymmetrical due to the quantum confinement effect, and fitting them with the Campbell-Fauchet method ^[85] is possible to obtain the average NW diameter for each used metal. Average diameters of 10 nm, 7 nm, and 5 nm were obtained by using 10 nm of Ag (red line), 2 nm of Au (blue line), and 3 nm of Au (green line), respectively. These diameters were further confirmed by an accurate statistical TEM analysis. These NW diameters are enough to present quantum confinement effect. The emission of all the samples is reported in <u>Figure 8g</u>, demonstrating their quantum confinement nature. In fact, the PL is redshifted by increasing the average diameter of the Si NWs, in perfect agreement with quantum confinement theory ^{[86][87]}.

A possible drawback for this MACE approach is the lack of order. However, the desired geometry that can be obtained by a masking procedure. However, this thin metal film approach is cost-effective to obtain vertically aligned and room temperature luminescent Si NWs.

Different metals were employed in these years as a catalyst during a MACE approach such as Ag [63][84][88][89], Au [65][86] [51][66], Pt [53], Ni [52], Cu [74], W [51]. The most used one remains the gold due to the best quality of fabricated Si NWs, for the stability in the etching solution compared to the silver, and for the fast and high tunable etching rate compared to other metals. Ti and other material such as AZO were also used as an adhesion layer for thick Au films, permitting to improve the film stability [77][78][90]. Kim et al. report the application of an Au/Ag bilayer mesh to avoid the issue on the Ag stability and anodic dissolution during the etching [63]. Wendisch et al. used an AZO reporting an improvement in the homogeneity of the etching and the possibility to vary the etching rate by changing its thickness ^[78]. The same group and also Yeom et al. $\frac{172}{1}$ report gold delamination for high H₂O₂ concentrations (e.g., for 10:1:10 HF/H₂O₂/H2O) and for in general high etch rates (>400-600 nm/m) and small thin films (<20 nm) [78]. The dependence on the etching rate is confirmed by other works [65] and it is reasonable to assume that metal instability may be also affected by the wafer pre-treatment and deposition type. The etching rate is the key parameter, and a too fast process can be unstable and not affordable in terms of reproducibility. Indeed, in our experiment using few nanometers of Au we never observed gold delamination or large area defects in the Si NW array by an etching rate of 460 nm/min and a solution of HF (5 M) and H₂O₂ (0.44 M). The role of a high concentration of H_2O_2 is clear because it can increase the hole injection and reaction at the metal silicon interface, thus increasing the bubble formation during the etching possibly affecting the metal stability. These effects and issues regard the use of a connected Au film.

The etching rate is influenced by the gold coverage and so by the NWs diameter. Indeed, the amount of silicon to be etched depends on the covered region of the gold template, on the pitches (average gold region between Si NWs), and on the diameter of Si NWs ^[78].

NW average diameter is determined by the metal film and usually ranges around 50 nm $\frac{[51][63]}{12}$ but as seen in <u>Figure 7</u> with the possibility to reach few nanometers and quantum confinement suitable dimensions $\frac{[12]}{12}$.

The reported preferential etching direction depends on several factors as wafer crystalline orientation, used etchant/oxidant solution, and its molar ratio, temperature, and metal film type and thickness $\frac{51}{71}$. The wafer crystalline orientation has been found as the main parameter that determines the etching orientation with a preferential etching along the <100> direction $\frac{38}{43}$. However, the concentration and ratio between the etchant and oxidant (usually HF/H₂O₂) can lead to other orientation etching. This can be understood considering that for a starting crystalline

orientation, the etching orientation is driven by the reaction kinetic. Starting from Si (100) it was demonstrated that <100> remain the etching direction at a low etching rate [63]. On the contrary, increasing the etching rate the same authors observed an etching in the <110> direction. The etching rate is characterized by the interplay of holes injection into silicon that is proportional to the metal electronegativity and to the oxidant H_2O_2 concentration and by the HF etching of silicon associated with the cleavage of Si back bonds [63]. Indeed, Si atom density exposed to the interface depends on the considered crystal plane [94]. At standard operation conditions, the hole injection is the limiting process of MACE. Increasing the concentration of injected holes above a certain threshold will cause the remotion of Si atoms where there is a higher concentration of Si back bonds causing in certain cases a change in the etching orientation. However, this condition requires a high enough HF concentration and the oxidant concentration as a limiting condition. Otherwise, with a Si (100) wafer, a low concentration of HF slowly etch the silicon in the <100> direction and the excess of holes diffuses causing new pore nucleation sites in presence of defect or doping atoms [51][63]. The temperature plays a role in the activation of non-<100> direction etching. Indeed, considering the same etching solution this can lead to an <100> etching at room temperature and <110> etching at higher temperatures (>50 °C for H₂O₂ 1 M and HF/H₂O₂ molar ratio of about 23) [63]. Temperature control is also used to low the etching rate and so the possible lateral etching with some works that report on cold MACE synthesis performed near 0 °C [65], while other works used higher temperature above 55 °C to form zigzag Si NWs [73].

As elicited, the type of metal mesh plays a role in the etching direction. Several experiments were performed in the same etching condition by using isolated metal particles instead of connected metal films. For metal film the etching is preferentially vertical to the wafer surface due to the difficulty of horizontal movement of the film. On the contrary, metal particles or isolated islands have more degrees of freedom. Indeed, MACE has been used to realize 3D etching taking advantage of the unconstrained metal particles movement during etching at the right conditions ^{[95][96]}.

Lateral etching or in general a more isotropic etching is found to happen when a large number of holes are injected at the metal-silicon interface $[\underline{66}][\underline{97}]$. The diffusion of these holes can oxidize the sidewall, and lead to a lateral etching and porous nanostructures. The porosity of Si NWs depends on the doping level of Si wafer and on the solution concentration, especially of H₂O₂ or other oxidant agents $[\underline{51}]$. Heavily doped Si wafers produce more easily porous Si NWs because the doping atoms may act as nucleation centers (e.g., metal atoms in solution), catalyzing the lateral etching and the pore formations $[\underline{98}][\underline{99}][\underline{100}]$. In highly doped substrates, a competition between vertical etching and lateral etching (and so porous formation) occurs $[\underline{101}][\underline{102}]$. If the vertical etching is fast enough it is possible to obtain crystalline Si NWs at the right bath condition without the formation of porous structure $[\underline{51}][\underline{84}]$. As for the crystalline orientation, there is a strong dependence on the ratio between the H₂O₂ (and so hole injection) and HF (and so Si atom remotion) $[\underline{51}]$.

Concerning the standard HF/H_2O_2 Mace bath Kim et al. reported that ethanol can be used to lower the etching rate influencing the etching direction and the final morphology ^[103]. This can also lead to tapered Si NWs as demonstrate by Azeredo et al. by controlling the ethanol concentration ^[104]. The addition of other oxidant co-solvent as methanol, isopropanol, acetonitrile, and so on has also been found as a method to change the etching orientation ^[103].

A final consideration is the possible agglomeration of the NWs tips as a result of a very high aspect ratio, and as a function of the drying protocol. Several works reported on the NW tips bunching for very long Si NWs ^{[65][40]}. A possible solution proposed in these years is a drying protocol that involves a final bath in isopropanol (lower capillary forces than water) followed by natural evaporation of the alcohol ^{[65][105]}. Bunching of micro and nanostructures are typical issues of MEMS. Hence another viable industrial solution for Si NWs or other microstructures is to use a critical point dryer ^{[27][106]}.

Metal film MACE permits a high flexibility of use for Si NW fabrication with several routes that can be followed to change diameter, orientation, density, porous formation, and so on. As demonstrated by the current trend of publications, the MACE method is becoming an outstanding tool for Si NWs synthesis and, for certain applications able to challenge RIE approaches for Si microstructure fabrication. In the next future, this relative novel approach may be really adopted for large-scale production of Si NWs thanks to the advantage of being compatible with the current industrial standard equipment. Indeed, the low-cost of this approach coupled with the very high aspect ratio makes it really appealing for microfabrication, challenging the more diffuse and consolidated approaches as DRIE.

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