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Toward scalable manufacturing of doped silicon nanopillars for thermoelectrics *via* metal-assisted chemical etching

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Metal-Assisted Chemical Etching (MACE) using Ag as the catalyst lets prepare vertically aligned crystalline silicon nanopillars (SiNPs), a highly promising system for thermoelectric applications, with high aspect ratios in a wide doping range. MACE may be implemented either by using Ag both as the catalyst and the oxidant (so-called one-pot MACE) or by using another chemical (typically H_2O_2) as the oxidant (two-pot MACE). This study investigates how the localized etching rate depends upon Si doping in both MACE implementations, accounting for the concurrent non-catalyzed etching. The latter, which shortens SiNPs, is found to become more significant in p-type Si at higher doping levels due to the narrower space-charge regions at the bare Si-solution interface. We demonstrated that in both one- and two-pot MACE the etching rate is controlled by the band bending at silicon−silver interface. In p-type silicon, it decreases with doping due to faster hole diffusion, while the Schottky barrier at the interface hinders hole injection in n-type silicon at any doping level. Overall, we highlight that MACE may be effectively implemented in its one-pot version, facilitating MACE scale-up toward SiNP large-scale manufacturing.

1. Introduction

In recent years silicon nanopillars have attracted considerable interest due to their unique and versatile properties. Their high aspect ratio, quasi-one dimensionality, inducing quantum confinement, and tunable electrical, thermal, and optical properties[1] make them suitable in several technologies. In photovoltaics, Si nanopillars (SiNPs) are used as absorbing layers[2] and as anti-reflective coatings.[3] They also found applications in sensing[4] and bio-sensing,[5] in photoelectrochemistry,[6] as electrodes in Li-ion batteries[7] and in energy storage.[8] Furthermore, SiNPs display a large thermoelectric figure of merit[9] compared to bulk single-crystalline Si (with a figure of merit of 0.01) due to the enhanced phonon scattering when their diameter is smaller than the phonon mean free path.[10–13] Thermoelectric modules based on SiNPs have been fabricated and characterized,[14,15] achieving figures of merit up to 0.24 at 700 K with a thermoelectric module where SiNP arrays were grown on both sides of a silicon wafer.[16]

Several techniques have been exploited to produce SiNPs, both bottom-up and top-down,[17] including Vapor–Liquid Solid,[18] Molecular Beam Epitaxy[19] and cryogenic Reactive Ion Etching.[20] However, they all require ultra-high-vacuum conditions, which severely limit their scalability. Additionally, the growth rate is low, also often resulting in low density SiNPs.[21]

Metal-Assisted Chemical Etching (MACE) provides a remarkable alternative, as it enables SiNP to be obtained at room temperature and ambient pressure with high densities, very high aspect ratios and excellent crystalline quality.[22] Moreover, MACE allows full control of SiNP orientation and, in principle, lets obtain SiNPs of arbitrary length. The technique is based on the local silicon oxidation catalyzed by metallic nanoparticles, which can be generated either *in situ* from a metallic salt or deposited *via* physical methods.[23] More specifically, when the metal acts both as the catalyst and the oxidant (*e.g.* using Ag/Ag⁺) the procedure is referred to as one-pot MACE. Instead, when the metal is used only as the catalyst while the oxidation is carried out by a different chemical (*e.g.* H_2O_2), it is known as two-pot MACE. blueOne-pot MACE is a simpler technque, as it does not require multiple solutions, thereby minimizing processing time and cost. In contrast, the two-pot MACE process follows a sequential approach, in which the catalyst nanoparticles are deposited on the Si surface (by either physical or chemical methods) prior to the etching step, at the cost of greater complexity. However, two-pot MACE

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Fig. 1 Cross section SEM images of n⁻ SiNPs obtained after 2-pot MACE reaction at differing etching time: 96 min (a), 192 min (b) 330 min (c) and 370 min (c).

To obtain a proper estimate of the MACE rate, one should consider that, in addition to MACE, etching also occurs on the bare Si surface, including SiNP tips. We will refer to this non-localized etching as *overetching*. Therefore, in what follows we first measured the dependence of overetching rate and its variation upon doping level and type; then, after measuring the apparent MACE rate, we corrected it accounting for the tip removal by overetching.

3.1. Overetching

The following results have been obtained performing both one-pot ([AgNO$_3$] = 16 mM and [HF] = 5 M) and two-pot ([H$_2$O$_2$] = 0.4 M and [HF] = 8 M) MACE.

By measuring the total thickness of the obtained samples, which includes the SiNP forests and the silicon layer beneath them, it is evident that the etched samples have a reduced thickness compared to the pristine silicon wafer (Fig. 2). This

thickness loss was observed for both MACE processes and for both doping types.

Thickness loss is evaluated as the difference between the pristine wafer thickness and the thickness of the samples, after MACE processes, for different reaction times. By plotting the thickness loss as a function of the reaction time, the overetching rate can be determined from the slope of the resulting line. The overetching rate as a function of the doping level for both n- and p-type silicon, and for both MACE processes, is reported in Fig. 3.

Overetching is more relevant in two-pot MACE than in one-pot and, moreover, the higher the doping level the higher the overetching rate for both p- and n-type substrates.

Two effects concur to such difference. From SEM analyses (Fig. 4) one observes the occurrence of etching pits on the tips and on the sidewalls of the wires. The formation of these additional localized etching sites arises from the reoxidation of metallic silver, with Ag⁺ subsequently undergoing reduction back to metallic silver. The redeposited Ag preferentially accumulates in energetically favorable regions and defects-rich sites such as the tips or walls of the nanopillars.[41]

Such *silver shuttling* is more pronounced in two-pot MACE. Indeed, in this case, silver nanoparticles located at the bottom of the bores can be oxidized by the hydrogen peroxide, which has a more positive redox potential than the Ag⁺/Ag couple (0.80 V and 1.78 V *vs.* SHE, respectively), and re-nucleate on the sidewall, reducing the effective length of the SiNPs.[42]

Silver shuttling is detectable also in one-pot MACE but the presence of the dendritic structures, which completely overfill the bores, partially hinders it, leading to a smaller thickness loss. Moreover in one-pot MACE the species that can re-oxidize silver is water, a weaker oxidant compare to hydrogen peroxide. Furthermore, in both one- and two-pot MACE, the presence of defects is higher in more heavily doped substrates, further promoting the formation of lateral etching sites,[43] in accordance with measured overetching rates (Fig. 3).
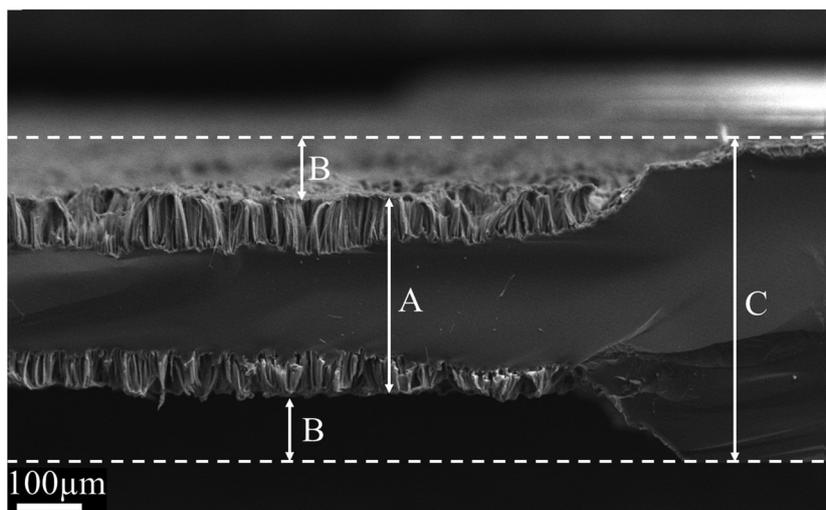
Fig. 2 Reduced thickness on p⁺ SiNPs obtained after one-pot MACE reaction (480 min). C is the pristine silicon wafer thickness, A is the overall thickness (SiNPs plus silicon membrane) after MACE and B is the material loss.
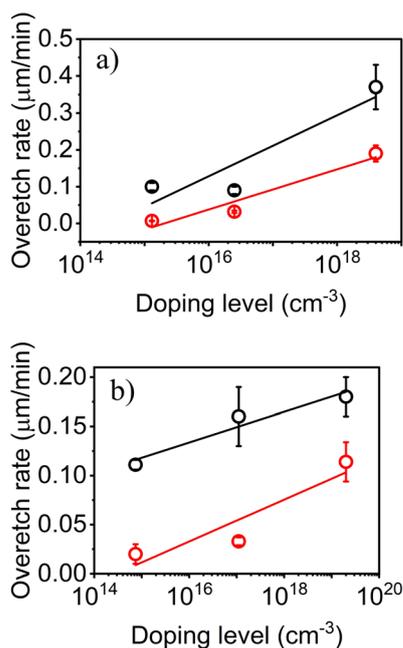
Fig. 3 Overetching rates *vs.* doping level for (a) p-type samples obtained with one-pot MACE (red) and 2-pot MACE (black). In (b) the rates for n-type samples obtained with one-pot MACE (red) and 2-pot MACE (black).

The second process that contributes to the thickness loss is the *non-localized* etching, basically the direct hole exchange between solution and silicon that occurs everywhere on the bare silicon surface. Non-localized etching always takes place and competes with localized etching,

being eventually dominant,[11,44] and occurs both in one- and two-pot MACE.

To better understand non-localized etching and its relation with silicon doping level, the interface between silicon and the oxidant solution is analyzed (Fig. 5 and Fig. S4).

In all cases, once contact is established and equilibrium conditions are reached, Fermi level of the semiconductor aligns with the redox potential of the oxidizing couple.[45,46] In one-pot MACE the interface is ruled by the Ag^+/Ag potential (Fig. 5) while in two-pot is determined by the H_2O_2/H_2O redox potential (Fig. S4). Since both the potential of Ag^+/Ag and H_2O_2/H_2O are more negative than the Fermi energies (Tables S1 and S2), bands always bend upward. Potential drop occurs almost entirely at the semiconductor side. In all cases, a potential barrier is formed at the silicon/solution interface. Thus, the injection of holes, from the solution into the valence band, and, consequently, their diffusion into the silicon bulk is hindered, leading to hole accumulation in the space-charge region near the silicon surface. The thickness of this space-charge region depends on the doping level and on the oxidizing strength of the redox couple. Specifically, the region narrows as the doping level increases. This is clearly noticeable in both Fig. 5 and S4. Indeed, in one-pot MACE the space-charge region in p^--type is approximately 800 nm wide, while in p^+-type is just 20 nm. A similar trend is observed for n^--type silicon ($\approx$1250 nm *versus* $\approx$12 nm in n^+-type) as shown in Fig. 5. Same behaviour can be observed in two-pot MACE for both silicon types (Fig. S4). Since the etching rate is correlated with the hole density near the silicon surface, a narrower space-charge region leads to a more pronounced overetching. This competes with localized etching, resulting in a more significant loss of thickness. Consequently, non-localized etching
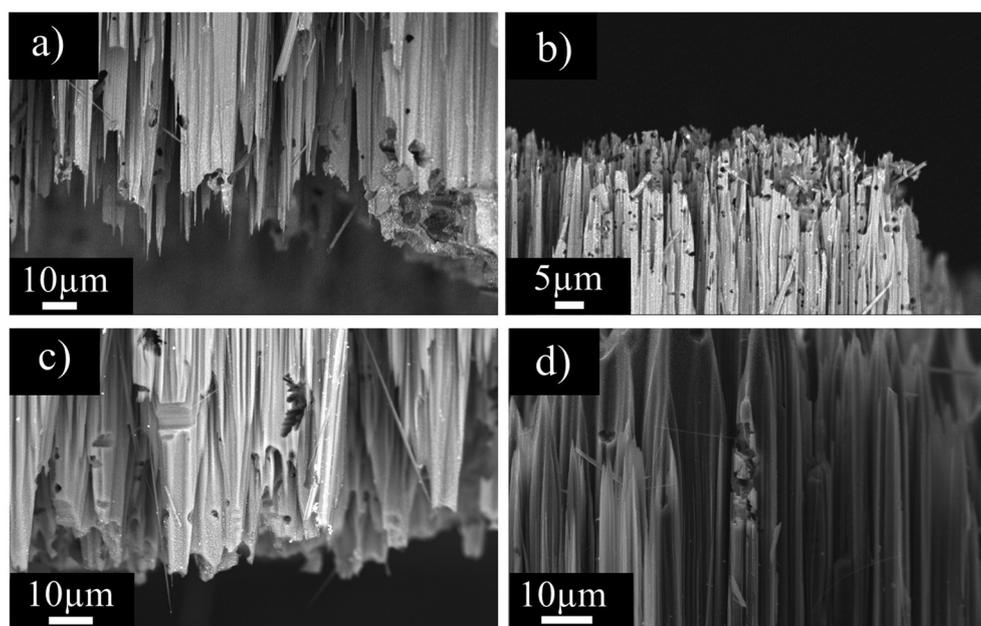
Fig. 4 Cross section SEM micrographs showing the effect of silver shuttling on the SiNP tips and sidewall. (a) and (b) on p-type SiNPs obtained with two-pot MACE and (c) and (d) on n-type SiNPs after one-pot MACE.
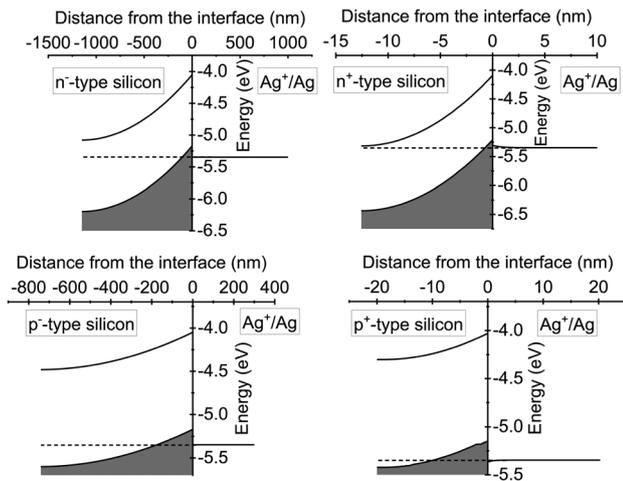
Fig. 5 Silicon band bending at equilibrium and at zero bias upon contact with Ag$^+$/Ag electrolyte solution, for p$^-$, p$^+$, n$^-$, and n$^+$ samples. The energy is referred to the vacuum level. Note that the space charge width decreases moving from low to high doped silicon, both for p- and n-type substrates.

is more prominent at higher doping levels, because the accumulation region is only a few tens of nanometers thick. In contrast, in lightly doped silicon, the accumulation region is wider, allowing diffusion of holes from the surface into the silicon bulk. This makes non-localized etching less effective, favouring the formation of SiNPs.

3.2. Localized etch rate

As it is known, in one-pot MACE silver nanoparticles are generated *in situ* from a silver salt, like AgNO$_3$, according to the electroless cathodic reduction:

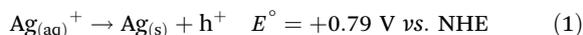$$Ag_{(aq)}^+ \rightarrow Ag_{(s)} + h^+ \quad E^\circ = +0.79 \text{ V } vs. \text{ NHE} \quad (1)$$

In this way metallic silver particles are deposited onto silicon surface and holes are injected into silicon valence band. Over time, these particles evolve in complex dendritic structures reaching a height of several microns. The dendrimers completely overfill the etching bores.[24] In the meantime, oxidation of silicon takes place. Two competing anodic reactions concurrently occur:[11,26] the first reaction is called 4-electron process and is the reaction ruling silicon electropolishing.[47] Silicon is directly oxidized to Si^{4+}:

$$Si_{(s)} + 4h^+ + 6H_2O_{(aq)} \rightarrow SiO_{2(s)} + 4H_3O^+$$
$$E^\circ = -0.84 \text{ V } vs. \text{ NHE} \quad (2)$$
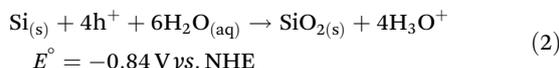
and subsequently SiO$_2$ is etched away by HF:

$$SiO_{2(s)} + 6HF_{(aq)} \rightarrow SiF_6{}^{2-}_{(aq)} + 3H_3O^+ \quad (3)$$
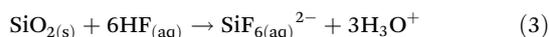
The alternative oxidation path is known as 2-electron process. In this case, silicon is initially oxidized to Si^{2+}:

$$Si_{(s)} + 2h^+ + 4HF_{(aq)} + 4H_2O_{(aq)} \rightarrow SiF_4{}^{2-}_{(aq)} + 4H_3O^+$$
$$E^\circ = -1.20 \text{ V } vs. \text{ NHE} \quad (4)$$
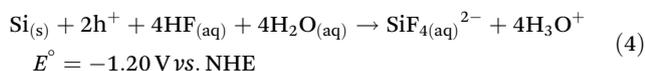
Then Si^{2+} is oxidized to Si^{4+} with the concurrent reduction of two hydronium ions to molecular hydrogen:

$$SiF_4{}^{2-}_{(aq)} + 2HF_{(aq)} \rightarrow SiF_6{}^{2-}_{(aq)} + H_{2(g)} \quad (5)$$

The 4-electron reaction is dominant for low-doped silicon substrates. In this case the oxide dissolution is the slow reaction step, leading to a smooth and regularly etched silicon surface or, when localized, to the formation of single-crystalline SiNPs. *Vice versa*, on highly doped silicon, 2-electron process prevails, the oxide elimination being the fast reaction step that leads to the formation of a porous silicon layer or, when localized, to (partially) porous SiNPs.[24]

Two-pot MACE occurs instead in two different steps.[48] First of all, the deposition of catalytic metallic nanoparticles takes place. This step could be performed either *via* chemical reduction of metallic cations in solution or by using physical methods like evaporation or sputtering. The second step is the silicon oxidation in a solution containing both the oxidant and HF. Typically, hydrogen peroxide (H$_2$O$_2$) is used as oxidant. Hydrogen peroxide injects holes into silicon according to the reaction:[26]

$$H_2O_{2(aq)} + 2H^+ \rightarrow 2H_2O_{(aq)} + 2h^+$$
$$E^\circ = +1.35 \text{ V } vs. \text{ NHE} \quad (6)$$
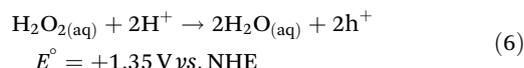
Oxidation of silicon and the oxide etching follow either the 4-electron or the 2-electron path, as in one-pot MACE.

Since the chemistry of one- and two-pot MACE is the same, one expects that etch rates should be comparable in the two processes. By plotting the SiNP lengths as a function of reaction time, the apparent localized etch rate for each doping level is obtained (Fig. 6), along with the effective etch rates. The latter was computed by taking into account the NP thickness loss due to overetching (Fig. 7). Essentially, the effective
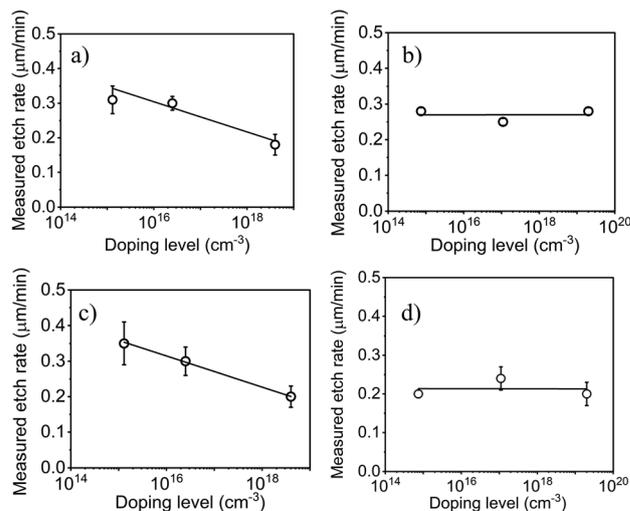
Fig. 6 Etch rates as function of the doping level. (a) One-pot MACE etch rate for p-type silicon and (b) for n-type silicon, while in (c) and (d) two-pot MACE etch rate for p- and n-type silicon respectively.
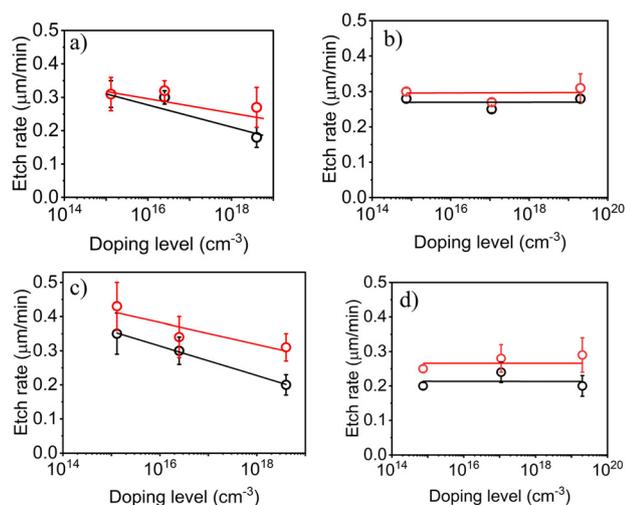
Fig. 7 Comparison between the apparent etch rate (black) and the effective one (red), computed considering the overetching, as function of the doping level for (a) one-pot MACE p-type, (b) one-pot MACE n-type, (c) two-pot MACE p-type and (d) two-pot MACE n-type silicon substrates.

Fig. 8 Band bending induced by the intimate contact between poly-crystalline silver and p-type silicon at different doping level: p^- (a), p (b) and p^+ SiNPs (c). The energy is referred to the vacuum level.

etch rate is the etch rate in the absence of overetching. As expected the effective etch rates are higher. The largest increase in the effective etch rate is noticeable for the highly doped samples. Nonetheless, in n-type samples, for both the one- and two-pot processes, the effective etch rate remains almost constant, confirming no dependence on the doping level. Instead, for p-type samples, the higher the doping level the lower the etch rate for both MACE processes.

Etch rate for p^- and p samples is similar, while at higher doping level it suddenly decreases for both one- and two-pot MACE. In contrast, in n-type samples the etch rate remains almost constant with varying doping levels. Thus, no qualitative difference in localized etch rate is observed between one-pot and two-pot MACE. Moreover, the SEM images in Fig. 1 and S1 show no noticeable morphological differences between the NPs obtained by one- and two-pot MACE.

To understand the different etching behaviour between n- and p-type silicon one should consider the interface between silicon and the catalytic metal (Fig. 8 and Fig. S3). When silver enters in intimate contact with silicon, Fermi level aligns with the metal work function, leading to a band bending in the semiconductor side – and to a potential drop thereof. The extent of band bending depends on the Fermi levels of the semiconductor (set by its doping level and type) and on the metal work function (4.26 eV for polycristalline silver[24]) (Fig. 8). This is manifestly the same in both one and two-pot MACE since bending depends solely on the relative position of the Fermi level and the silver work function, which are not affected by the oxidant species. Thus, the localized etch rate is ruled by the silicon/silver interface.

For all doping level the presence of metallic silver pins the Fermi energy and the band folds downward. Thus, no potential barrier hindering hole injection into the valence band and
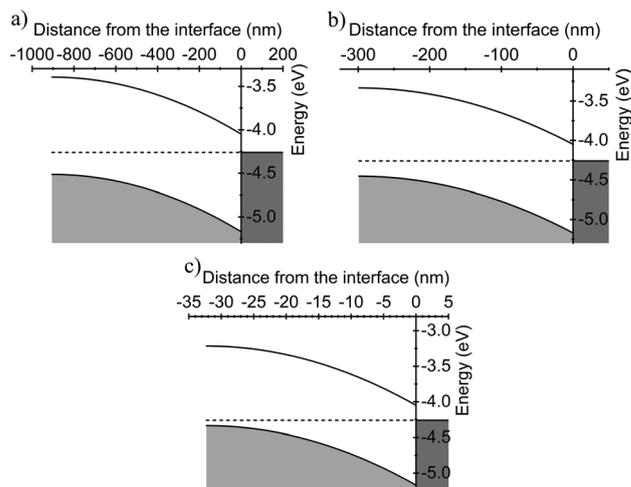
their diffusion toward silicon bulk is present. According to Lai et al.,[29] who observed similar results in two-pot MACE using gold as a catalyst, in p-type silicon the absence of a potential barrier means that the concentration of holes is ruled by their drift velocity away from the interface. The drift velocity, in turn, depends both on the hole mobility and on the electric field strength at the interface. As doping increases, mobility decreases while the electric field increases, since at higher doping level the space-charge region narrows, dropping from ≈900 nm in p^- samples to ≈300 nm in p samples and to just ≈33 nm in p^+ Si. Therefore, p^- and p samples exhibit similar drift velocities and, as a result, comparable etch rates. Instead, in p^+ silicon, the electric field strength becomes dominant, compensating for the reduced mobility. Thus, holes move away from the interface, causing a lower etch rate.

In the case of n-type silicon (Fig. S3), while for lightly doped samples there is a slight downward band bending, in samples with higher doping levels, the bands bend upwards, displaying the formation of a potential barrier at the silver/silicon interface. The barrier, in the case of n and n^+ Si, opposes to the injection of holes into silicon valence band confining the holes near the interface. Consequently, the etch rate is similar regardless of the doping level.

It is worth mentioning that when the silicon/silver system is immersed in the solution, another interface is also formed, namely the one between silver and the electrolyte solution. The potential drop that occurs at the interface can be computed using the classical metal/solution interface and can be described with the standard electrical double layer model.[49] However, the calculated potential drop at the Ag/electrolyte interface is significantly smaller than that at the Si/Ag interface and therefore does not affect the silicon band bending and does not play a relevant role in the MACE mechanism. This is in agreement with literature reports.[45,46] Further details on the band bending calculations and interface modeling are reported in the SI.

4. Summary and conclusion

In this study we investigated the etch rate as a function of silicon doping type and concentration, also accounting for the overetching phenomenon. The latter consistently reduces the effective SiNP length. The impact of overetching becomes more pronounced with increasing doping level, independently of dopant type. This behavior was attributed to the simultaneous enhancement of silver shuttling and non-localized etching under high doping conditions. Indeed, in highly doped silicon the increased density of defects facilitates silver shuttling by promoting the dissolution and re-nucleation of metallic silver on SiNP tips and sidewalls. Moreover, silver shuttling is generally more pronounced in two-pot MACE process compared to one-pot. This is due to the higher oxidative potential of H_2O_2 (1.77 V *vs.* SHE) which can re-oxidize metallic silver more easily than O_2 and H_2O (1.23 V *vs.* SHE) in one-pot MACE. Additionally, the space-charge region at the silicon/electrolytic solution interface becomes significantly narrower in highly doped substrates, increasing the hole density near the silicon surface and favoring non-localized etching. As a result, the overall SiNP length loss becomes more substantial. This trend highlights the critical need to account for overetching when precise control over SiNP length is required, particularly in highly doped silicon substrates.

When analyzing the effective etch rate, which includes losses due to overetching, no substantial difference is observed between one-pot and two-pot MACE. This indicates that the etching is primarily governed by the silicon/silver interface through the doping level and type of the semiconductor. In p-type silicon, where silver does not form a Schottky barrier, the etch rate decreases with doping concentration due to the fast hole diffusion away from the interface. In highly doped p-type samples the reduction in hole mobility is compensated by the increased electric field strength at the interface, resulting from the narrower space charge region compared to low-doped samples. This stronger field accelerates hole drift away from the interface, preventing effective participation in the etching reaction and thus reducing the etch rate. In contrast, for n-type silicon, the presence of a Schottky barrier at the interface hinders hole injection, resulting in an etch rate largely independent of doping level. These findings are in agreement with Lai *et al.*[29] and Backes *et al.*[31,32] who observed similar results in two-pot using both gold and silver as catalyst. Notably, our study extends this understanding to include one-pot MACE, showing that even with different oxidant environments, the same doping-dependent trends hold on, confirming the key role of the silicon/silver interface in governing the etch rate.

In conclusion, this study provides deeper insight into the fundamental mechanisms governing MACE for different doped silicon type. By demonstrating that the etch rate is ruled by interfacial processes at the silicon/silver junction, rather than by the type of MACE process, we simplify the choice between one-pot and two-pot strategies for various applications. This flexibility is particularly valuable for scalable manufacturing of SiNPs. Additionally, the role of overetching is highlighted as a critical factor affecting final SiNP length, especially in highly doped silicon.

Author contributions

FG: writing – original draft, review & editing, investigation, formal analysis, conceptualization, methodology. LC: investigation, formal analysis. FA: investigation. AB: investigation. DN: writing – review & editing, conceptualization, methodology, project administration, funding acquisition, supervision.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article, including the etch rate showed in Fig. 3, 6 and 7, are available at Bicocca Open Archive Research Data at https://board.unimib.it/datasets/bk82wc727y/1, https://doi.org/10.17632/bk82wc727y.1.

Supplementary information (SI) is available. See DOI: https://doi.org/10.1039/d5nr03474d.

Acknowledgements

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