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Highlights:

- A method combining metal-assisted chemical etching and machine learning is proposed to fabricate sub-10 nm nanopore arrays on silicon wafers with various dopant types and concentrations.
- The relationship between nanopore structures and fabrication conditions is modeled and experimentally verified.
- A processing parameter window for generating regular nanopore arrays on silicon wafers with variable doping types and concentrations is obtained.

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Achieving a sub-10 nm nanopore array in silicon by metal-assisted chemical etching and machine learning

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Abstract

Solid-state nanopores with controllable pore size and morphology have huge application potential. However, it has been very challenging to process sub-10 nm silicon nanopore arrays with high efficiency and high quality at low cost. In this study, a method combining metal-assisted chemical etching and machine learning is proposed to fabricate sub-10 nm nanopore arrays on silicon wafers with various dopant types and concentrations. Through a SVM algorithm, the relationship between the nanopore structures and the fabrication conditions, including the etching solution, etching time, dopant type, and concentration, was modeled and experimentally verified. Based on this, a processing parameter window for generating regular nanopore arrays on silicon wafers with variable doping types and concentrations was obtained. The proposed machine-learning-assisted etching method will provide a feasible and economical way to process high-quality silicon nanopores, nanostructures, and devices.

Supplementary material for this article is available online

Keywords: sub-10 nm silicon nanopore array, metal-assisted chemical etching, silica-coated gold nanoparticles, self-assembly, machine learning

1. Introduction

Solid-state nanopores with controllable pore size and morphology have huge application potential in the fields of DNA sequencing [1], sensors [2], and nanofiltration [3]. However, processing large-area, regular solid-state nanopore arrays has been very challenging. At present, the mainstream methods for processing solid-state nanopores include ion beam/electron beam drilling and engraving methods [4, 5], reactive ion etching assisted by electron beam lithography [6], and metal-assisted chemical etching (MACE) [7–9]. Among these methods, MACE overcomes many limitations of traditional wet and dry etching technologies because of its controllable etching direction, simple fabrication setting, low processing cost, and high efficiency and has thus been widely used in...
controllable processing of various micro-nano structures, such as nanopores and nanowires [10–14]. It is possible to realize directional etching by tuning the catalysts’ shape or the etchant, enabling both high aspect ratio one-dimensional nanostructures [15] and three-dimensional nanostructures [16] to be facilely fabricated.

In recent years, extensive research has been conducted on improving the fabrication capabilities of MACE techniques. For instance, Kim et al combined photolithography with MACE to fabricate a regular silicon (Si) pore array with a diameter larger than 100 nm [17]; however, this process requires expensive photolithography equipment. Since the fabrication resolution is limited by the mask, it cannot process sub-10 nm nanopore arrays. Grossman et al sputtered silver nanoparticles (NPs) on a Si wafer surface and then used MACE to process nanopores with an average diameter of 13.5 nm [18]. Further decreasing the nanopore size in a controllable fashion would require a precise size definition of the sputtered silver NPs. To this end, Patil et al developed a direct current magnetron sputtering process for depositing precious metal NPs on a Si wafer surface [19]. Nguyen et al annealed a layer of 0.4 nm silver film that was deposited on Si by electron beam evaporation [20] and then achieved sub-10 nm nanopores through MACE, but the nanopores were randomly distributed because the sputtering and annealing process could not define the position of the NPs. To address this issue, Grossman et al used a self-assembly method to obtain close-packed, silica-coated AuNP arrays and successfully processed sub-10 nm nanopores using MACE [21]. The group further modified the colloid composition by combining silica NPs and silica-coated gold NPs of the same diameter and drop-casted the colloid on a Si wafer to create a single-layer ordered array, which allowed for successful processing of more sparsely distributed nanospheres, approximately 20 nm in diameter, through MACE [22]. While this approach is very promising for creating nanopores with controllable size and spacing, it has to be realized through a fabrication protocol with highly efficient optimization capability and high reproducibility due to the complex physical and chemical processes involved in self-assembly and etching.

Most previous studies using MACE have adopted empirical rules for optimization of the fabrication process, which is time-consuming and largely processing-environment-dependent. In recent years, machine learning (ML) techniques have been introduced into the manufacturing industry [23]; and combining first principles with material experiments has been shown to provide important guidelines for the exploration and development of new materials [24–27]. In particular, given the recent success in applying ML regression models to guide the fabrication of organic electronics [28, 29], ML is expected to be a promising and cost-efficient method of guiding MACE of nanostructures.

In this work, an ML method based on a support vector machine (SVM) algorithm is proposed to explore and optimize the multidimensional parameter space of MACE processing in generating sub-10 nm pore arrays on various Si wafers (figure 1), including N and P types with different doping concentrations, as they are equally important in the semiconductor industry. SVM offers unique advantages and outstanding performance in solving problems with small sample, nonlinear, and high-dimensional recognition patterns [30]. Through the analysis and training of the experimental results obtained following the process shown in figure 1(a), an SVM-based ML classification model was developed and experimentally verified, which then enabled the achievement of sub-10 nm pore arrays by MACE on various Si wafers. The underlying mechanism that governs the critical pore formation process can be described through hole carrier concentration-determined band bending at the gold nanoparticle/silicon (AuNP/Si) interface.

2. Materials and methods

2.1. Self-assembly of silica-coated AuNPs

A 4 inch monocrystalline Si wafer (crystal orientation (100), purchased from Hefei Zhaoru Optoelectronics Technology Co., Ltd, China) was cut into small pieces of 5 by 5 mm². The characteristics of the Si wafers were as follows: lightly doped N-type (N) wafer with a resistivity of 1–10 Ω cm and a thickness of 500 ± 25 µm; moderately doped N-type (N+) wafer with a resistivity of 0.01–0.05 Ω cm and a thickness of 500 µm; heavily doped N-type (N++) wafer with a resistivity of less than 0.001 Ω cm and a thickness of 500 µm; lightly doped P-type (P) wafer with a resistivity of 5–10 Ω cm and a thickness of 500 ± 25 µm; moderately doped P-type (P+) wafer with a resistivity of 0.01–0.05 Ω cm and a thickness of 500 µm; a heavily doped P-type (P++) wafer with a resistivity of less than 0.001 Ω cm and a thickness of 500 ± 10 µm.

The Si samples were cleaned in absolute ethanol and an ion water (DI water) ultrasonic bath for 3 min each, respectively, and dried with a nitrogen (N) flow. Then, the Si samples were processed in a plasma flow for 10 min to enhance the surface wetting ability.

The solution containing silica-coated gold (Au@SiO₂) NPs (purchased from Sigma-Aldrich, USA) was processed under ultrasonic conditions for 3 min. Then, using a pipette, 2.5 μl of the Au@SiO₂ NP solution were directly dropped on the Si sample, which was fixed on a spinner. The spinner was first run at a speed of 300 rpm for 5 s and then at a speed of 2000 rpm for another 5 s to form a uniform monolayer film on the sample. After that, the spinner was run at a speed of 5000 rpm for 9 s to remove the excess solution. The Si sample was then allowed to stand for 3 h to completely evaporate the solution. Finally, a single layer of close-packed Au@SiO₂ NPs was obtained on the Si sample surface. These processes were all carried out in a clean room with the temperature and humidity strictly controlled at 23 °C and 50%, respectively.

2.2. MACE of sub-10 nm cavities in Si

After self-assembly processing, the samples were immersed in the etchant containing 15 ml of hydrofluoric acid (HF, 49 wt.%) (RHAWN), X ml hydrogen peroxide (H₂O₂, 30 wt.%) (Aladdin), and (17–X) ml of DI water (18.2 MΩ cm) (Milli-Q from Millipore). The etching time (t min) was varied according to the experimental conditions. Then the etched
samples were rinsed with a large amount of DI water for about 15 s and dried with a compressed N flow for about 15 s.

2.3. Characterization

A field emission transmission electron microscope (FETEM) (F200S, Talos) was used to characterize the Au@SiO$_2$ NPs, and the diameter of the Au@SiO$_2$ NPs and the core gold nanoparticles (AuNPs) were measured. A FESEM (SU8220, Hitachi) was used to characterize the self-assembly of Au@SiO$_2$ NPs and etched Si samples.

3. Results and discussion

3.1. Typical morphology evolution during etching

Figure 2 shows the typical method that was used to process a nanopore array on a moderately doped N-type Si sample by MACE with self-assembled Au@SiO$_2$ NPs. The single-layer, close-packed array formed on the Si sample by Au@SiO$_2$ NPs assembling is shown in figure 2(a). Further, the Au@SiO$_2$ NPs were characterized by FETEM, as shown in figure 2(b), which shows the diameter of the core AuNPs was about 5 nm; and the outer diameter of the Au@SiO$_2$ NPs was about 28 nm; as such, the pitch between the two AuNPs after forming a close-packed array was around 28 nm.

Once the etching solution containing HF was introduced, the outer silicon dioxide (SiO$_2$) coating was completely dissolved, and the inner AuNPs gradually settled to the Si sample surface (figure 2(c)), forming a relatively uniformly distributed AuNP pattern. Subsequently, a nanopore array started to evolve as the AuNP array was etched into the Si sample. For instance, with a H$_2$O$_2$ volume of 0.7 ml in the etching solution and an etching time of 8 min, a nanopore array can be formed, as shown in figure 2(d). From the cross-section, it can be seen that the etching direction was almost vertical with a depth of approximately 63 nm (figures S1(b) and (c) in supplementary data files (available online at stacks.iop.org/IJEM/3/035104/mmedia)). Figure 2(h) shows the statistics and analysis of the Si nanopore. The average diameter of the 1000 nanopores counted was 9.0 nm, and the standard deviation was 1.5 nm. After normal distribution fitting, the upper and lower limits of the 95% confidence interval of the average diameter were 9.1 nm and 8.9 nm, respectively, suggesting uniform cavity distribution. It is noted that the diameter of the nanopores was slightly larger than that of the AuNPs. This may have been caused by the drift/diffusion of the hole carriers generated by the gold-catalyzed reduction of H$_2$O$_2$ during the etching process. As a result, the nearby surrounding regions (e.g. sidewalls) were also oxidized to form SiO$_2$ and subsequently etched by HF, in addition to the area in direct contact with the AuNPs. Figure 2(i) shows the statistical analysis of the pitch between the Si nanopores. The average pitch of adjacent nanopores was 25.1 nm, and the standard deviation was 4.7 nm. After normal distribution fitting, the upper and lower limits of the 95% confidence interval of the average pitch were 24.2 nm and 26.0 nm, respectively, which is slightly smaller than the average nanopores of Au@SiO$_2$ NPs. The result was consistent with the pitch of the AuNPs. The slightly larger distribution deviation in the pitch may have been due to the interference of external etching fluid flow and uneven temperature distribution causing some of the AuNPs to shift slightly away from their original positions.

It is important to note that the morphology of the nanopore arrays was closely related to the etching conditions. For instance, no nanopores were formed when the volume of H$_2$O$_2$ was only 0.1 ml, even if the etching time was extended to 30 min or 60 min. In this case, the AuNP array was not etched into the Si sample, as shown in figure 2(c). Such a scenario is referred to as ‘unetched’. On the other hand, if the etching time was extended to 20 min for an etching solution with 0.7 ml
H$_2$O$_2$, the same process resulted in significantly increased nanopore sizes or interconnected nanopore structures, as shown in figure 2(e) and figure S1(c) in supplementary data files, which is referred to as ‘overetched’. Similarly, when the H$_2$O$_2$ volume was increased to 1.0 ml while the etching time was kept as 8 min, porous structures were also obtained (figure 2(f)); the etching direction became random (figure S1(d) in supplementary data files) as the high energy provided by the extensive H$_2$O$_2$ reduction promoted etching in other crystal directions other than the <100> direction; and further increasing the etching time would lead to severe overetched results, such as sponge-like porous structures (figures 2(g) and S1(f) in supplementary data files). These results suggest that unoptimized H$_2$O$_2$ volume and etching time could easily lead to unetched or overetched results. Therefore, an accurate and efficient prediction method for the proper etching conditions should be developed for well-controlled sub-10 nm nanopore fabrication.

3.2. Modeling the MACE processing using ML

Due to the complex physical and chemical processes involved in nanopore fabrication, it is difficult to rely on a traditional design of experiments (DOE) to determine the fabrication conditions required to achieve the targeted nanopore diameter and pitch. Therefore, an SVM classification model was applied to predict the MACE process for sub-10 nm Si nanopore array fabrication. Figure 3(d) shows the process of specific ML modeling. According to our experimental experience, the volume of HF in the etchant has little effect on the etching. Therefore, the volume of HF used in all of the experiments presented in this research was fixed at 15 ml. As shown in table 1 and figure S2 in supplementary data files, a multilevel design was carried out for the other four parameters (etching solution, etching time, dopant type, and concentration); and a total of 380 sets of experiments were carried out (figure 3(a)). As the combinations of these parameters cannot fully cover all of the conditions that affect the etching directions, vertical etching is not explicitly considered in the parameters training of the model. According to the structures shown in figure 2, the results of MACE processing of nanopore arrays can be divided into three types: unetched, ideal result, and overetched, based on the nanopore shape. The results obtained were divided into training data and test data, and the SVM algorithm based on the cubic kernel function was used to classify and train the training data. Tenfold cross-validation with the test data was performed to reduce overfitting and statistical error resulting from artificial sampling. The detailed training process of the specific model parameters is shown in section 1 in supplementary data files. As can be seen from the confusion matrix diagram (figure 3(b)), the accuracy of the trained model for all classification prediction results was above 90%, indicating that the model’s classification results fit well with the experimental data.
Figure 3. Determining the optimal etching solution by using the ML method. (a) Original data; (b) confusion matrix of the trained model; (c) normalized significance of each parameter on the sub-10 nm nanopore array etching; (d) ML algorithm used; (e) typical phase digraph of sub-10 nm nanopore array etching on P + Si predicted by the ML model.

| Parameters/factors | Parameter range | Levels |
|--------------------|-----------------|--------|
| Dopant type        | N-doped, P-doped | 2      |
| Dopant concentration| Light, Medium, Heavy | 3      |
| Volume of H₂O₂ (ml) | 0–6             | 40     |
| Etching time (min)  | 1–30            | 22     |

Table 1. Multilevel DOE.

To further determine the influence of the Si wafer dopant type, dopant concentration, H₂O₂ volume, and etching time on the etching process, the method of evaluating the reduction in the model accuracy after removing a single factor [31] was used. Figure 3(c) shows the contribution of the process parameters to the etching process. It was found that among all of the factors, the volume of H₂O₂ had the greatest impact on the processing of Si nanopore arrays, followed by etching time and doping concentration. The dopant type of Si sample had the least impact.

To better determine the distribution range of the process parameters of the three different types of experimental results, the prediction results of the SVM classification model were sliced and visualized, as shown in figure 3(e). In order to not lose generality, the predicted results of processing nanopore arrays on P + Si samples were selected for analysis; and it was found that the overetched results accounted for most of the parameter space, followed by the unetched area. The suitable parameter area of ideal results occupied only a small part. That is to say, the process parameter window of the proper Si nanopore array was very narrow. Compared with other works (table S3 in supplementary data files), the use of ML to model the MACE process can effectively find the process parameter combination that meets the required processing quality, which is useful for accelerating the processing development.

Figure 4 shows the visual prediction results of processing the nanopore arrays on Si samples of different dopant types and concentrations. It can be seen that no matter the Si sample used, P-type or N-type, the dopant concentration in the Si samples increased when other conditions were unchanged, the parameter distribution range of the overetched results greatly increased (figures 3(e) and 4(a)–(e)), and the parameter distribution range of the ideal and the underetched results were correspondingly reduced, especially the ideal one which only accounted for less than 5% of the entire area of the parameter distribution range (figure 4(f)). It can also be found that with an increase in the doping concentration, the relative area of the ideal results for the P-type Si samples decreased faster than those of the N-type Si samples (figure 4(f)), indicating that processing of nanopore arrays in P-type Si samples was more sensitive to the doping concentration.
3.3. Experiment validation of the ML predicted results

Next, the results of the ML predictions were verified by experimenting with the etching processing parameters selected from figure 4. Figure 5 shows the results of nanopore processing on lightly and heavily doped N-type Si samples. Consistent with the ML model, when lightly doped N-type Si samples were etched in an etchant containing 0.5 ml of H$_2$O$_2$ for 30 min, no microstructures appeared on the Si samples. After the SiO$_2$ shell was dissolved by the HF in the etchant, the AuNPs in the core settled on the Si sample surface, forming a relatively uniformly distributed AuNPs array (figure 5(a)). When H$_2$O$_2$ content in the etchant was increased to 4.0 ml, but the etching time was shortened to 5 min, a uniformly distributed array of nanopores was processed on the Si sample as predicted (figure 5(b)). When any single factor of H$_2$O$_2$ content and etching time exceeded the appropriate process parameter window predicted by the ML model, such as when the etching time was extended to 15 min or the H$_2$O$_2$ content was increased to 6.0 ml, overetched structures appeared. Porous structures with adjacent nanopores were formed on the Si sample (figures S4(c) and (d) in supplementary data files). Obviously, when both the volume of H$_2$O$_2$ and the etching time exceeded the appropriate process parameter window predicted by the ML model, for example, when the H$_2$O$_2$ content was increased to 6.0 ml and the etching time was extended to 15 min, a more severe overetched sponge-like porous structure was formed (figure 5(c)).

The same situation also occurred in the etching of the heavily doped N-type Si sample. Unetched (figure 5(d)), ideal (figure 5(e)), and overetched (figure 5(f)) structures appeared, as expected, on the Si samples when the etching parameters selected from figure 4 were used. The transition states from the ideal to overetched structures are shown in figures S4(c) and (d) in supplementary data files. Figure 6 shows the results of fabricating nanopores on P-type Si samples with different dopant concentrations. Also, unetched (figures 6(a), (d), and (g)), ideal (figures 6(b), (e), and (h)), and overetched (figures 6(e), (f), and (i)) structures appeared unexpectedly on the lightly, moderately, and heavily doped P-type Si samples, respectively. The transition states from ideal to overetched structures are shown in figure S5 in supplementary data files. The accuracy of the MACE ML model in predicting the effects of H$_2$O$_2$ volume and etching time was higher than 98% and 95%, respectively (table S1 and S2 in supplementary data files). The consistency of the ML predictions with the experimental results demonstrates the accuracy of the ML model and guarantees repeatability.

3.4. Etching mechanism and discussion

From the ML predictions and the actual experimental results, it was found that for a Si wafer, whether P-type or N-type, an increased doping level requires a decreased H$_2$O$_2$ concentration in the etchant to create a regular nanopore array.
Figure 5. Processing of nanopores on N-type Si samples based on ML predictions. Lightly doped N-type Si samples were etched in (a) etchant containing 0.5 ml of H$_2$O$_2$ for 30 min; (b) etchant containing 4.0 ml of H$_2$O$_2$ for 5 min; and (c) etchant containing 6.0 ml of H$_2$O$_2$ for 15 min. Heavily doped N-type Si samples were etched in (d) etchant containing 0.1 ml of H$_2$O$_2$ for 30 min; (e) etchant containing 0.5 ml of H$_2$O$_2$ for 8 min; and (f) etchant containing 1.0 ml of H$_2$O$_2$ for 20 min. The scale bars are all 50 nm.

This phenomenon can be explained as follows: the higher the dopant concentration, the shorter the length of the depletion layer formed between the AuNPs and the Si samples, resulting in more serious band bending (figure 7, the detailed calculation process is shown in section 2 in the supporting information). Thus, hole carriers, which are generated by the H$_2$O$_2$ reduction catalyzed by AuNPs, are conducive to accumulation in the position where AuNPs contact with the Si sample, so as to increase the hole carrier concentration at this position and promote the occurrence and rate of the etching reaction [32, 33]. On the other hand, the higher the dopant concentration, the more defects are introduced in the crystal lattice [34]; and the etching reaction is likely to occur at the doped site. It was also found that under the same doping concentration, the H$_2$O$_2$ content required for processing different Si samples was different. The H$_2$O$_2$ content required for processing regular nanopore array in N-type doped Si samples was lower than that of P-type doped Si samples [33, 34], indicating that the N-type doped Si sample was more sensitive to the concentration of H$_2$O$_2$.

The ML results also provide us with some insights on how the etching conditions should be holistically designed. Firstly, excessive volume of H$_2$O$_2$ usually results in overetched porous structures. Secondly, with the increase in the doping concentration of the Si sample, the volume of H$_2$O$_2$ required to process a regular nanopore array is sharply reduced, indicating that the volume control of H$_2$O$_2$ should be more stringent during the etchant design. Generally, prolonging the etching time is likely to cause overetched results. However, with the increase in the doping concentration, the appropriate volume of H$_2$O$_2$ that can obtain a regular nanopore array is decreased, resulting in a slower etching rate; therefore, the etching time window becomes appropriately larger. The use of instruments, such as pipettes, during processing can well control the volume of H$_2$O$_2$; but it is very difficult to accurately control the etching processing time because of the multiple steps involved in taking out samples, cleaning, and drying as well as the difficulty in realizing rapid removal of residue etchant in the nanopores. Therefore, it is vital to accurately control the etchant composition when processing sub-10 nm Si nanopore arrays using MACE so as to leave a certain time margin for process operations, thereby reducing the processing difficulty.

4. Conclusion

In summary, this work demonstrated the first attempt to combine ML with MACE to process regular sub-10 nm nanopore arrays on Si wafers with various dopant types and concentrations. The results show that the SVM-based ML model can well map the relationship between the nanopore structures and the fabrication (etching solution, etching time, dopant type, and concentration). Using the model, the processing parameter window for generating regular nanopore arrays on various types of Si wafers was identified and experimentally verified. The study also revealed that although the suitable processing parameter window is very narrow, uniformly distributed and well-shaped sub-10 nm nanopore arrays on all kinds of Si samples can be obtained using MACE by precisely controlling the H$_2$O$_2$ content in the etchant and the etching time. In general, it was found that the etching results on P-type Si wafers were more sensitive to the doping concentration while those
Figure 6. Processing of nanopores on P-type Si samples based on ML predictions. Lightly doped P-type Si samples were etched in (a) etchant containing 0.5 ml of H$_2$O$_2$ for 30 min; (b) etchant containing 3.0 ml of H$_2$O$_2$ for 4 min; and (c) etchant containing 5.0 ml of H$_2$O$_2$ for 20 min. Moderately doped P-type Si samples were etched in (d) etchant containing 0.3 ml of H$_2$O$_2$ for 30 min; (e) etchant containing 1.5 ml of H$_2$O$_2$ for 8 min; and (f) etchant containing 3.0 ml of H$_2$O$_2$ for 20 min. Heavily doped P-type Si samples were etched in (g) etchant containing 0.1 ml of H$_2$O$_2$ for 30 min; (h) etchant containing 0.7 ml of H$_2$O$_2$ for 8 min; and (i) etchant containing 1.0 ml of H$_2$O$_2$ for 20 min. The scale bars are all 50 nm.

Figure 7. Band bending diagram of the Au and Si (100) interface. (a) Geometry model and (b) averaged Hartree difference potential energy and projected local density of states of the interface. Both of them demonstrate the Schottky barrier height was about 0.7 eV which is very close to the experimental one (0.76 eV) [35]. (c) Effects of dopant concentration on the band diagram. The band was bent more severely when the dopant concentration increased.
on the N-type Si wafers were more sensitive to the H₂O₂ concentration, which can be associated with different band bending properties at the AuNP/Si interface. These fundamental insights and the new ML-based fabrication protocol demonstrated in this study provide useful guidelines for controllable processing of sub-10 nm nanopore arrays in Si wafers and other related semiconductor materials.

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Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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