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Automated and inexpensive method to manufacture solid-state nanopores and micropores in robust silicon wafers

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Abstract. In this work an easy, reproducible and inexpensive technique for the production of solid state nanopores and micropores using silicon wafer substrate is proposed. The technique is based on control of pore formation, by neutralization etchant (KOH) with a strong acid (HCl). Thus, a local neutralization is produced around the nanopore, which stops the silicon etching. The etching process was performed with 7M KOH at 80°C, where 1.23 μ m/min etching speed was obtained, similar to those published in literature. The control of the pore formation with the braking acid method was done using 12M HCl and different extreme conditions: i) at 25°C, ii) at 80°C and iii) at 80°C applying an electric potential. In these studies, it was found that nanopores and micropores can be obtained automatically and at a low cost. Additionally, the process was optimized to obtain clean silicon wafers after the pore fabrication process. This method opens the possibility for an efficient scale-up from laboratory production.

1. Introduction

Nanopore-based technologies are emerging as a powerful tool for single molecule analysis. They can be used in different applications such as detection of ssDNA [1-3], dsDNA segment [4-6] and proteins [7,8]. Micropores have been used as well to detect cancer cells [9]. The production of solid state nanopores has aroused great interest because silicon wafers are inexpensive, resistant and durable. In particular, solid state nanopores included inside the wafer are easy to handle and show great resistance to washing (including sonication) when compared to nanopores made on silicon nitride/dioxide membranes, which are extremely fragile and must be handled carefully. Normally, the methods to produce solid-state nanopores involve the use of advanced microscopy tools to complete the manufacturing process, namely Transmission Electron Microscopy (TEM) [10], Scanning Transmission Electron Microscopy (STEM) or Focused Ion Beam (FIB) [11]. However, the most traditional methods for making nanopores in silicon wafers involve standard microfabrication tools such as photolithography for pattern definition and Reactive Ion Etching (RIE) to remove the silicon nitride layer on the exposed area. This work describes a method to manufactured pores up to 20nm diameter which relies on automatic braking pore formation, without the intervention of an external agent. Nanopores and micropores were manufactured using KOH etching and subsequently chemical braking was performed with HCl, in order to automatically control the pore opening. Chemical breaking is accomplished as the neutralizing acid HCl becomes in contact the basic etchant KOH through the nanopore.



2. Materials and methods

2.1. Pattern formation

A schematic picture of the pattern forming process is shown in Figure 1. The substrates used were $700\mu\text{m}$ thick double-side polished $\langle 100 \rangle$ oriented silicon wafers (Virginia Semiconductor Inc.). A silicon nitride layer 50nm thick was deposited on a wafer using Plasma Enhanced chemical vapour deposition (PECVD) at 600°C . The gas used for plasma deposition was hexamethyldisilazane $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ and nitrogen as reactive gas.

2.2. Chemical etching

The chemical anisotropic etching of silicon wafers was carried out using 7M KOH at 80°C . First, the etching was performed simultaneously on both sides of the silicon wafer. The reaction was stopped before the inverted pyramids joined. Subsequently, the silicon wafer was removed from the container in which the first etching was performed and the wafer was washed with deionized water and introduced into a PDMS device, where a second etching step was performed (chemical braking). The pore size was adjusted by controlling the reaction temperature and / or applying an electric potential. Fifteen samples were studied for each condition. Chemical braking was performed at two temperatures: 25°C and 80°C . These two temperatures were chosen to study, according to previous studies [12] where the greater rate of nanopores formation was obtained. A potential of 12V was also applied to control the reaction rate. At this stage KOH 4M and HCl 12M was used, being a simple neutralization reaction, where the HCl is used in excess to ensure the OH^- neutralization.

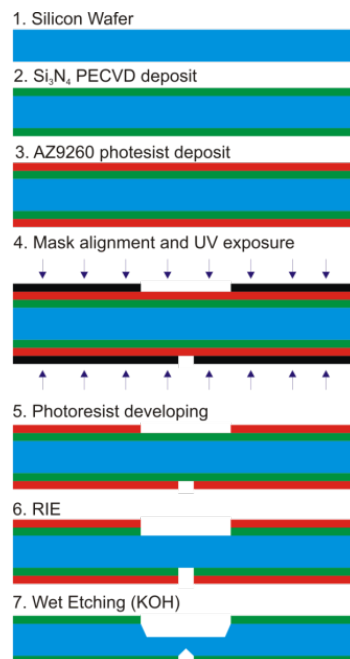


Figure 1. Steps for the manufacturing process of nanopores on a silicon wafer.

3. Results

Figure 2 shows the results of the etch depth versus time for the three studied processes. In the three cases, the joining of the two cavities produces an abrupt chemical braking of the etching process. However, only in cases of chemical braking at 25°C and 80°C with applied voltage it was possible to

obtain nanopores. Additionally, in all cases the braking reaction occurred when a window depth of approximately $510 \pm 2 \mu\text{m}$ was achieved.

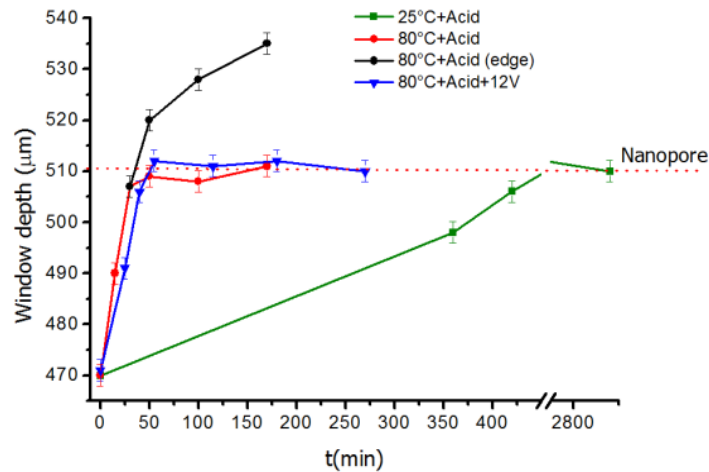


Figure 2. Comparison of the window depth of 2.1mm, according to the attack time for the three procedures studied.

Figure 3(a) and 3(b) shows a nanopore and micropore respectively, obtained by this technique. Thus, HCl protons have more time to traverse the newly formed nanopore and neutralize the KOH. So, the etching stops and allows nanopore formation. Micropores can be produced if the second etching step is allowed to continue further, because as the pore opening increases, the acid braking process cannot be sustained. The silicon nitride layer is degraded, exposing the underlying silicon. It was found that after about 3300 minutes etching micropores are formed, which will be larger with longer etching times.

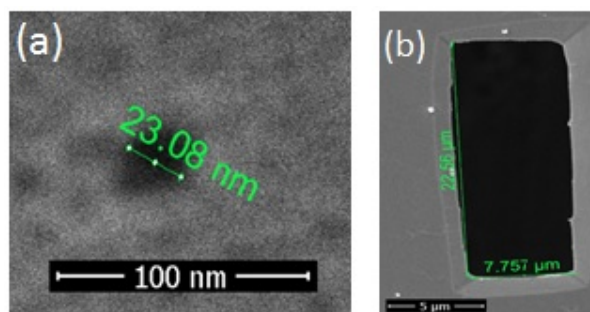


Figure 3. (a) Nanopore SEM image obtained by etching combined with braking acid, 4M KOH at room temperature and (b) Micropore SEM obtained by etching with 4M KOH and 12M HCl, at room temperature after 4000 minutes.

The application of electric potential also has the advantage of acting as a cleaning process of the wafer surface. In cases in which the etching agent and the braking agent which can react to form salts crystallize or precipitate, applying a potential attracts ions to the electrode, leaving the substrate surface free of ions or crystals. This process is useful for industrial application, because it avoids the need for extensive subsequent washes. Figure 3 shows two wafers treated with the braking acid at 80°C temperature. In the wafer of Figure 4(a), a 12V potential was applied and in the wafer of Figure 4(b), potential was not applied. On the wafer on which the potential was applied, the surface was

completely clean and free from reaction products. The other wafer (no applied voltage) shows a white precipitate on the surface, corresponding to KCl that formed upon neutralization.

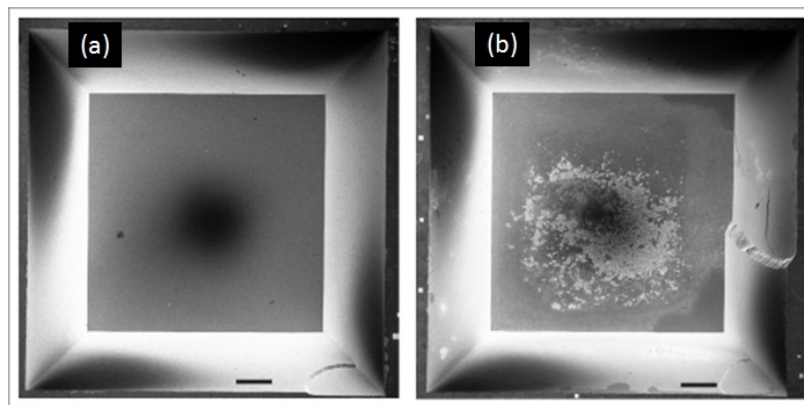


Figure 4. Windows formed in silicon wafers etched with acid braking method. (a) With electric potential. (b) No electrical potential. The scale bar in both images represents 200 μ m.

4. Conclusions

The results presented here for the manufacture of nanopores with chemical braking method have shown several advantages over other manufacturing methods. First, the method allows to stop the nanopore manufacturing process automatically, without any feedback system or the intervention of an external agent. It is also possible to obtain micropores, if the second etching process has longer exposure time. Over 200 minutes for 80°C experiments, 250min for 80°C with applied voltage experiments and finally 2800 minutes at room temperature experiments. Second, this process has a low cost compared to other manufacturing methods which require the use of FIB and e-beam. For this reason this method can be very useful for the development of new technologies for biomolecules sensing using nanopores, providing an easily adaptable methodology to mass production processes at low cost. This paper introduces a new concept for the manufacture of nanopores and micropores, demonstrating that the proposed method works and defines a direction for future work. An extensive characterization of the method as well as the study of nanopore arrays production will be the subject of future publications.

Acknowledgments

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