Fabrication and characterization of Si nanotips utilizing anisotropic wet etching

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ABSTRACT

Nano tips are important structures for various applications such as topography measurement, Microfluidics, and microelectronics. There are different approaches to develop the silicon nano tips. In this study a simple, low cost and non toxic method to obtain nano tips using anisotropic wet etching is proposed, where 30% KOH (Potassium Hydroxide) was used as etchant with the addition of IPA (Isopropanol) to improve the surface roughness. The profile and topography of the fabricated nanotips were evaluated by SEM and Confocal microscopy. Anisotropic KOH wet etching is validated as simple, fast and inexpensive method to achieve nano pyramidal tips with 467.8 nm tip diameter with a tip height of 20 µm.

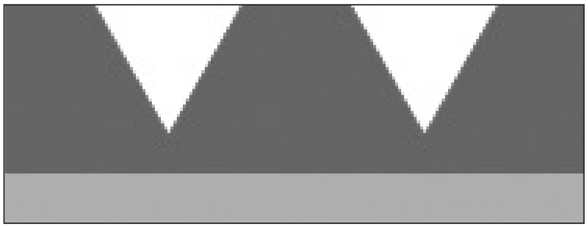
KEYWORDS

KOH,
Si Nano Tips,
Silicon,
Wet Etching.

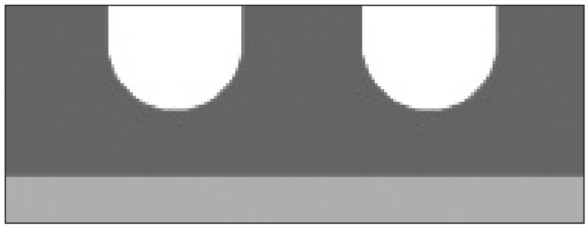
1. Introduction

In recent years, the field of nanotechnology has witnessed remarkable advancements, particularly in the fabrication of nanoscale structures with diverse applications in electronics, photonics, and biotechnology. Among various nanostructures, nanotips have garnered significant attention due to their potential in high-resolution imaging, sensing, tip-enhanced spectroscopy, flat panel displays, field emission electron guns, ultra speed switches, field emission diodes, highly sensitive sensors, atomic force microscopy (AFM) microprobes and various micro-electromechanical system (MEMS) devices. The ability to precisely control the geometry and morphology of nanotips is crucial for optimizing their performance in these applications (Alves et al., 2005; Resnik et al., 2003).

Silicon Nanotips can be formed by employing various techniques such as reactive ion etching (RIE) and wet etching each with its own set of advantages and challenges. Dry etching techniques, while effective in producing fine features, can be expensive and may lead to issues such as surface roughness and non-uniformity. Whereas, wet silicon etching is performed using various chemical etchants which defines the anisotropic and isotropic etch profiles as depicted in fig 1. In wet isotropic etching the etching occurs equally in all directions using the etchant hydrofluoric nitric acetic (HNA), in order to achieve sharp pyramidal tips orientation dependent anisotropic wet etching is considered with different concentrations of strong alkaline etchants such as potassium hydroxide (KOH), sodium hydroxide (NaOH), and Tetramethylammonium hydroxide (TMAH). In this study KOH is used as etchant due to its non toxic nature and high etch rate as compared to the other etchants discussed above (Resnik et al., 2003; Tang & Sato, 2011; Abidin et al., 2015; Sheu et al., 2001).



(a) Anisotropic wet etching



(b) Isotropic wet etching

Fig. 1. Etching profiles.

Silicon tips are important structures required for these applications. Si micro and nano pyramidal tips are formed using orientation dependent anisotropic etching, factors such as tip sharpness, uniformity, and aspect ratio of the microtip are

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important parameters to be considered from the point of microprobe robustness and sample assessment. Typically microprobes with high aspect ratio tips are required in AFM to scan rough profiles that change abruptly (Resnik et al., 2003).

The anisotropic etching occurs as a result of different crystal orientations of Si, Si (100) surface orientation shows better etching results as supposed to Si (111) which feebly etches under KOH with the ratio of 400:1 (Abidin et al., 2015), this is explained by the orientation of Si atoms. As dangling bonds are quite active, Si (100) has two dangling bonds which are readily hydroxylated whereas Si (111) has one dangling bond and all the back bonds are attached to neighboring atoms with no dangling bonds due to which it gains extra stability against wet etchants like KOH (Choi et al., 2022; Monteiro et al., 2015). The nano tips are formed by utilizing the characteristic (110) and (111) 54.7° angled planes (Abidin et al., 2015).

As the etching process proceeds the Si atoms are hydroxylated which requires both OH^- and H_2O species. The Si-H bonds are replaced by the hydroxyl (OH^-) groups of KOH forming silicates with the release of H_2 gas bubbles (Abidin et al., 2015; Chen et al., 2002; Monteiro et al., 2015). The overall reaction is given below,

$$Si + 2\,OH^- + 2\,H_2O \rightarrow 2\,SiO_2\,(OH)_2^{2-} + 2\,H_2 \quad ....(1)$$

The KOH etch characteristics are influenced by incorporating additives such as isopropyl alcohol (IPA), which influences the etch rate and morphology of the nano tips. By integrating IPA into the KOH etching process the uniformity and sharpness of nanotips will be improved. By comparing this approach with other nanotips fabrication techniques, this research aims to highlight the benefits of KOH wet etching in terms of process simplicity, cost-effectiveness, and scalability (Sheu et al., 2001; Monteiro et al., 2015).

2. Experimental Procedure

Experiments were performed on 4 inch Silicon wafer of p-type with (100) crystallographic orientation and it was thermally oxidized at 1200°C to an oxide thickness of 1 µm which served as etching mask. The following process flow as shown in fig 2 was followed to achieve nano tips.

2.1. Photolithography

The mask for photolithography was designed using CleWin software as shown in fig 3. Square mask (40 x 40 µm^2, 30 x 30 µm^2, 20 x 20 µm^2) array was designed. Prior to photolithography process, general cleaning was carried out, where the sample was rinsed in acetone, IPA and DI water for 1 minute each followed by dehydration bake at 100°C for 5 minutes to remove any surface impurities.

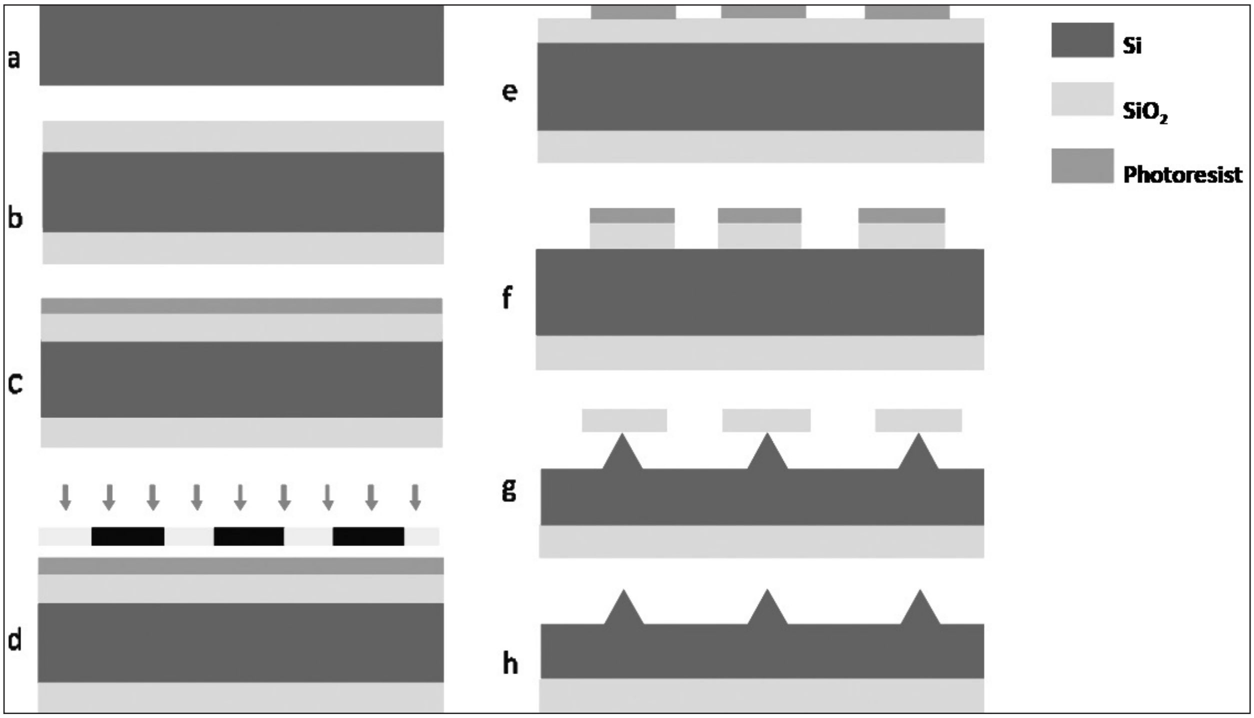


Fig. 2. Fabrication process flow, (a) Si wafer (b) SiO_2 deposition (c) AZ 1518 photoresist spin coating (d) exposure (e) development (f) SiO_2 dry etching (g) Si wet etching (h) BOE SiO_2 etching.

Spin coating was done using AZ 1518 photoresist (PR) since it has strong adhesion on SiO_2 substrate after the soft-baking process even without any adhesion promoting agent. The PR coating thickness achieved depends on the spin coating parameters like speed of rotation and time, which can be referred in the Photoresist manufacturer datasheet. Here, 4000 rpm spin coating rotation is selected to achieve a 2 µm thickness, which is optimum to withstand 30 minutes of anisotropic Si wet etching on SiO_2 mask. The PR coated sample is soft baked at 110°C for 90 seconds to improve the stability and adhesion of the Photoresist.

Post soft bake patterns were transferred onto the substrate using Direct Laser Writer (DLW) photolithography, microtech, Taiwan. The laser exposed patterns are developed using 1: 4 ratio of AZ 351B developer and DI water. The development occurs at the exposed area by stripping off the PR and leaving the unexposed patterns behind. Post development bake (hard bake) is done at 110°C for 90 seconds to increase the stability of the PR for further wet etching processes.

Prior to KOH wet etching of Si, Dry etching was employed to selectively remove SiO_2 layer using ICPRIE (Inductively Coupled Plasma Reactive Ion Etching) process.

2.2. Anisotropic Si wet etching

The etching solutions were prepared from analytical grade KOH pellets, sigma aldrich., India and isopropyl alcohol (IPA). To perform anisotropic etching 30 %(w/v) KOH solution was prepared and was heated to 80°C under reflux condenser after the exothermic reaction between KOH and water cools down. The reaction temperature was limited by the boiling point of isopropanol (82°C), 10 % (v/v) Isopropanol (IPA) was added to the etching solution after it reaches 80°C. Addition of IPA reduces the surface tension of KOH and increases the wettability of hydrophobic Si which aids in smooth etched surface with reduced hillocks. On the downside IPA decreases the etch rate as the IPA molecules get adsorbed on Si surface which hinders the access of reactants (i.e. OH^- anions and H_2O molecules) to the etched surface.

30% KOH concentration at 80°C temperature is chosen for this work as it provides high etch rate while maintaining surface smoothness during the Si etching process. The etch rate of Si is expected to be 1 µm/min and that of SiO_2 mask layer is 5nm/min at the said concentration and reaction temperature. The reaction was carried out under reflux condenser, 30% (w/v) KOH solution was prepared in a beaker to which required volume of IPA was added and the solution was heated to 80°C with constant stirring at 300 rpm under water bath to maintain constant temperature throughout the reaction. The Si substrate in a wafer holder was placed in the beaker containing the etchant under a reflux condenser. The reaction set up was placed on a hot plate with magnetic stirrer attachment. Constant stirring is required to remove the H_2 gas bubbles that are produced as a reaction byproduct from the Si surface which causes surface roughness and reduces the etch rate. After the etching process the substrate

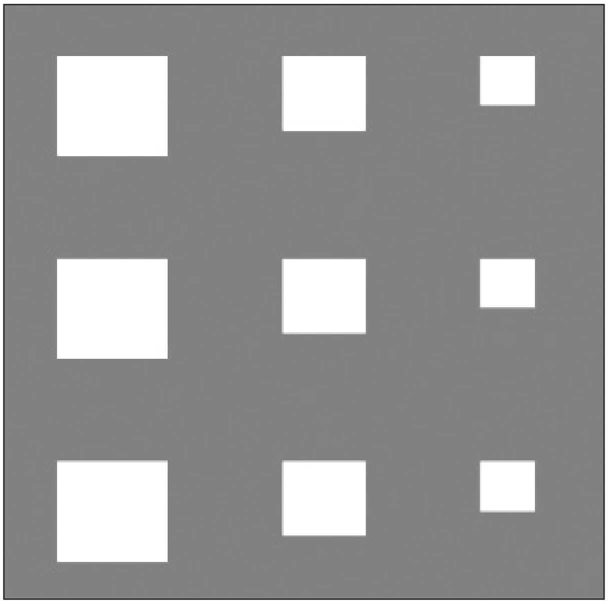


Fig. 3. 40 x 40 µm^2, 30 x 30 µm^2, and 20 x 20 µm^2 mask patterns.

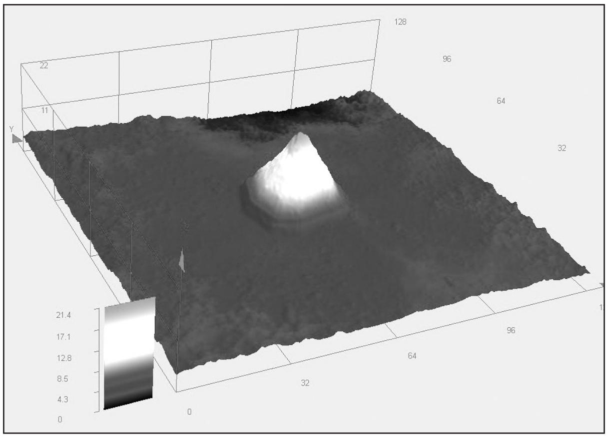
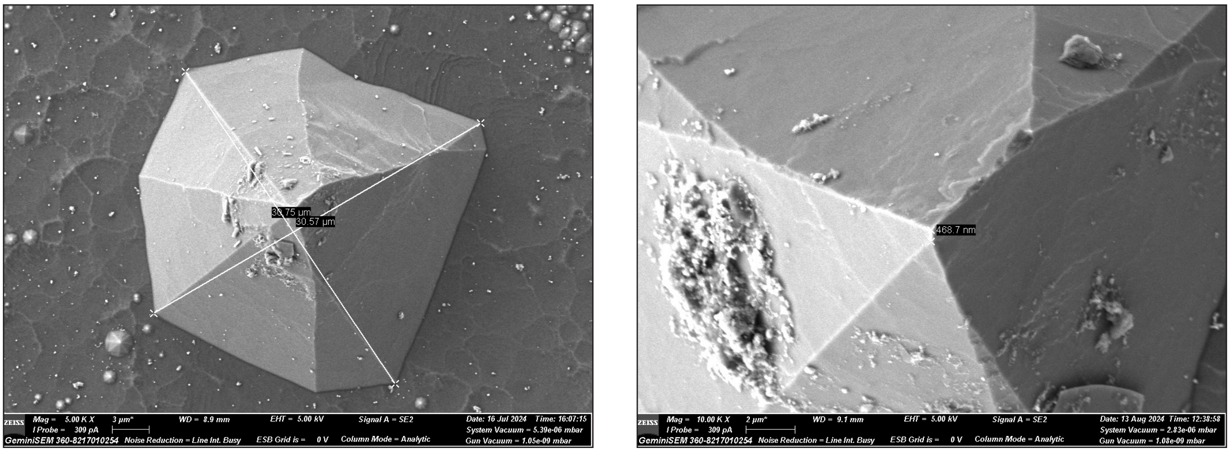


Fig. 4. Confocal microscopy of a nanotip where height is 20 µm.



(a) (b)

Fig. 5. (a) SEM imaging of a nano tip, (b) length of the nano blade.

is rinsed in DI water for 5 minutes to remove any residual etchant and dried using N_2 shown in fig 2 (g). The SiO_2 mask layer present on the nano pyramidal tips is removed using BOE (buffered oxide etchant) as shown in fig 2 (h) followed by DI water rinse and drying using N_2 gas.

3. Results and Discussions

The boiling point of 30% KOH is 100°C and that of IPA is 82°C, due to which the upper limit for temperature during KOH wet etching is set at 80°C. Moreover beyond 80^{o}C surface roughness and hillocks were observed on Si surface. The etch rate of Si depends on the concentration of KOH and the reaction temperature. It is seen that at lower concentrations like 10% - 20% KOH, the etch rate is relatively higher but results in rough etched surfaces. For KOH concentrations above 30% the Si etch rate decreases as the concentrations are increased. The addition of IPA improves the surface roughness by decreasing the stability of hydrogen bubbles that settle on the surface acting as micro masks.

Optical microscope was used to determine the progress of the reaction in an interval of 10 minutes, the etching process was carried out for 20 minutes. Fig 4, shows Confocal microscopy results for the nano pyramidal tips that are formed, where the tip heights of 20 µm, 13 µm, and 8 µm were achieved for the dimensions 40 x 40 µm^2, 30 x 30 µm^2, and 20 x 20 µm^2. The sidewall surface and the tip diameter of the etched nano tips were examined using SEM imaging, where the tip formed has an edge to it forming a blade kind of structure fig 5 (b), because all the faces involved in forming the needle do not converge at the vertex, giving rise to a nano blade. The length of the blade formed is 467.8 nm.

4. Conclusion

The study involved fabrication of nano tips using square masks of 40µm, 30µm and 20µm diameter. Upon etching the Si substrate using 30% KOH + IPA resulted in octagonal pyramidal nano tip, at the vertex nano blade structures were observed under SEM, because all the faces that form the tip did not converge at a point leading to the blade structure. Further studies and modifications are required to achieve a sharp nanotip without the formation of blade structures. Upon which these nano tips can employed as microprobes for AFM and other applications.

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