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Difference in Activated Atomic Steps on (111) Silicon Surface during KOH and TMAH Etching

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Anisotropic etching of (111) silicon surface using potassium hydroxide (KOH) and tetra-methyl ammonium hydroxide (TMAH) solutions was experimentally investigated. Etching advanced as a result of lateral movement of steps of 20–50 nm in height. Steps on the (111) surface are classified into two groups, those that are perpendicular to $[11\bar{2}]$ and, those that are perpendicular to $[\bar{1}\,\bar{1}\,2]$. Steps having a three-backbonded edge were more stable than those having a two-backbonded edge in case of KOH etching. On the contrary, in case of TMAH, steps having a three-backbonded edge were more active than steps having a two-backbonded edge. This fact explains the difference in macroscopic anisotropy in KOH and TMAH etching in the vicinity of (111).

1. Introduction

Anisotropic etching of single-crystal silicon has been widely used for fabricating micromechanical devices. However, the fundamental mechanism of anisotropic etching is less understood than application techniques. Anisotropy has been simply discussed based on the difference in the number of dangling bonds appearing on the silicon surface that is assumed to be perfectly flat. This is the main reason for misguidance of the discussion. Atomic-scale material removal during etching was rather recently observed on silicon surfaces by probe microscopy,[1] and a theoretical discussion has recently been initiated for the etching of the (111) surface. van Veenendaal[2] studied the etch rate anisotropy for vicinical silicon (111) surface based on the kinetic smoothing model. Hines[3] and

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Munford, *et al.*[4] independently argued that linear atomic steps exist on the (111) surface, and the material removal advances as a lateral movement of these steps. Steps are classified into two groups, those which are perpendicular to $[11\bar{2}]$ and those which are perpendicular to $[\bar{1}\,\bar{1}2]$. Silicon atoms on the edge of those two types of step have different numbers of backbonds, i.e., two and three, respectively. They also argued that the step with a three-backbonded edge is more stable than that with a two-backbonded edge. Thus they explained the reason why triangular mesa or dimples surrounded by linear steps were observed on the (111) surface during NH_4F etching. On the other hand, in a macroscopic domain, Nijdam, *et al.*[5] observed hexagonal etch pits growing on the (111) surface during potassium hydroxide (KOH) etching, and found that dislocations are the origin of the etch pits.

The purpose of this study is to xamine the (111) surface during etching under the most commonly used conditions using KOH and tetra-methyl ammonium hydroxide (TMAH) solutions. Because of the difficulty of *in-situ* observation using a probe microscopy system under such severe etching conditions, we observed the surface *ex-situ* in time increments. We found an etching mechanism similar to that of atomic level mentioned above. At the same time, we found that such steps on the (111) surface are differently activated according to the difference in etching solution, regardless of the number of backbonds of the atom located at the step edge. Contrary to the results with NH_4F etching and an etching model based on the number of backbonds at the step edge, three-backbonded steps were etched faster with TMAH solution than two-backbonded steps. We verified our findings by observing the difference in the macroscopic etching behavior of silicon between the two etchants.

2. Experimental Method

We observed the shapes of shallow etch-pits growing on the silicon (111) surface during etching. The sidewalls of the etch pits are regarded as a cluster of atomic steps moving in lateral directions. We measured the size and growth rate of the shallow etch-pits.

We used (111) silicon chips cut out of p-type CZ wafers. The wafer was doped with boron resulting in the resistivity of 10 Ω-cm. The surface of the wafer was mirror-polished as received from a wafer supplier. We introduced seeds of etch-pits by the following method. The wafer was first oxidized at 1100°C for 20 h. This results in a surface oxide layer 3 μm thick. The oxide was then completely removed by BHF etching for 30 min.

We etched (111) silicon chips under two different conditions (1) and (2) as below.

(1) 40 wt%KOH water solution at 70°C.

(2) 25 wt%TMAH water solution at 80°C.

The etching rates for (100) silicon under the two conditions were almost equal.

We observed the (111) surface in time increments, and watched the changes in shape and size of a single etch-pit during etching. The total time of etching was 30 to 40 min. The etching was interrupted every 10 min, and silicon chips were rinsed and dried before every observation. Such interruption in the successive etching steps had little influenced on the surface morphology. This was unlike the case of etching of the (110) surface, where the

morphology significantly changed due to the interruption of etching.

We used an optical microscope, a 3D surface profiler (Zygo, NV5010), and an AFM system (Topometrix, Explorer) for the observation.

3. Results and Discussion

3.1 *Etch-pit growth on (111) silicon*

We observed a number of etch-pits on a (111) surface, which had experienced heavy oxidization and removal of the oxide prior to etching. Figure 1 shows an optical image of the etch-pits which have hexagonal contours as reported by Nijdam, *et al.*[5] The sides of the hexagon were aligned to $[11\bar{2}]$and $[\bar{1}\,\bar{1}\,2]$ as occurs in the atomic scale models.[3, 4]

From AFM observation of the etch-pit, it was clarified that the pits are shallow, and the sidewalls have step-and-terrace structures. Figure 2 shows an AFM image at the center of

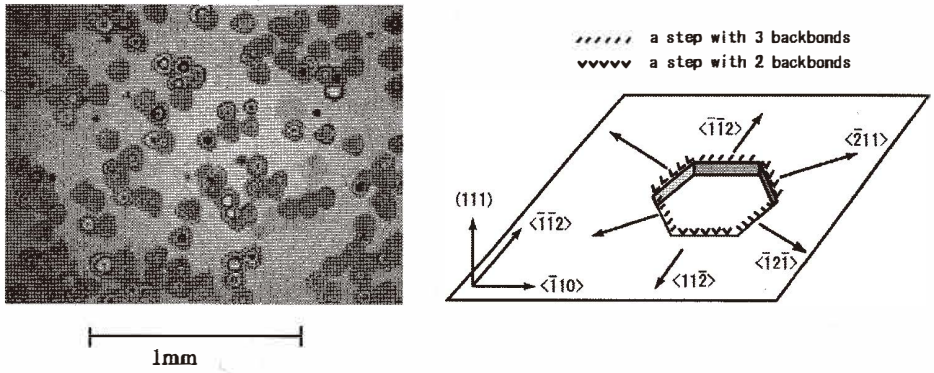

Fig. 1. Shallow etch-pits on a silicon (111) surface, and its schematic contour.

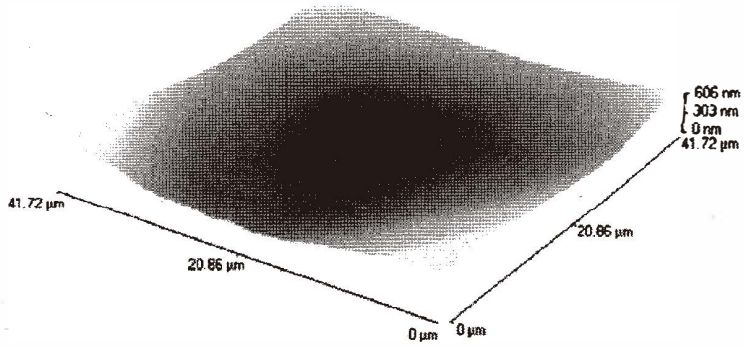

Fig. 2. AFM image at the center of the pit etched with TMAH.

the pit etched with TMAH solution. The step height was on the order of 20–50 nm, which is regarded as a cluster of atomic steps. Compared to the previously reported atomic-scale observations with NH_4F etching, the step height is much larger however, in both cases, the pits had hexagonal contours and tended to become triangular.[3, 4]

The observed cross-sectional growth of the etch-pit is typically shown in Fig. 3. The cross section was measured in time increments using a 3D surface profiler. Both diameter and depth of the pit proportionally increased with an increase of etching time. The increase in the depth saturated when the depth reached 1–2 μm, while the diameter of the pit increased linearly. On the other hand, in case of wafers not subjected to oxidization prior to etching, the etch-pit depth stopped to increase much earlier at the depth of 0.2 μm or less as shown in Fig. 4. In addition, the etch-pit density was far less than that of oxidized wafers. This means that the heavy oxidization gave seeds of etch-pits deep into a wafer on the order of 1 μm.

The gradient of the sidewall equals the ratio of lateral step velocity to the increase in etch-pit depth. We estimated lateral step velocity as being more than 100 times larger than the increase in pit depth. The lateral step movement obviously dominates the etching rate of (111) silicon, as long as steps exist on the (111) surface. It was also observed that the gradients of sidewalls in Fig. 3 are in asymmetry, when comparing opposite sidewalls. This means that opposite sidewalls having different types of steps show different growth velocities in lateral directions. In fact, the top view of the pit is not in symmetry as shown in Fig. 5. This is explained by the difference in the nature of step edges between steps aligned to $[11\bar{2}]$ and $[\bar{1}\,\bar{1}\,2]$ as mentioned before.

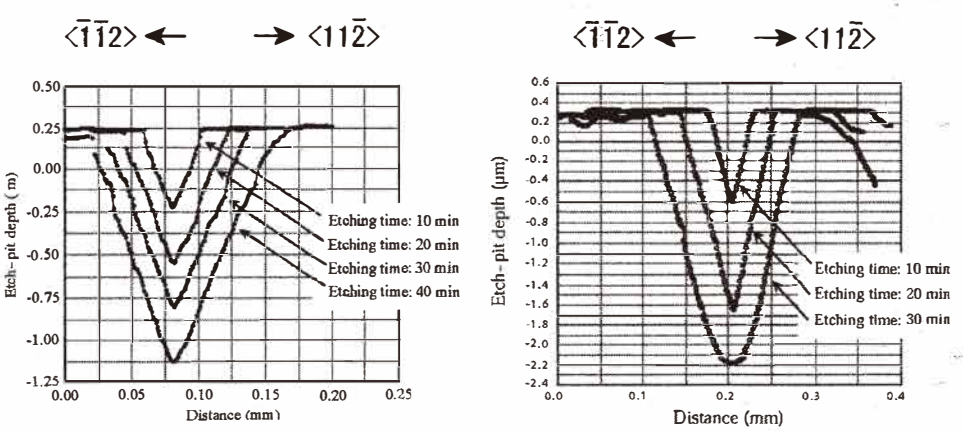

Fig. 3. Change in etch-pit cross section showing linear growth observed on heavily oxidized wafer etched in (a) 40% KOH at 70°C, and (b) 25 wt% TMAH at 80°C.

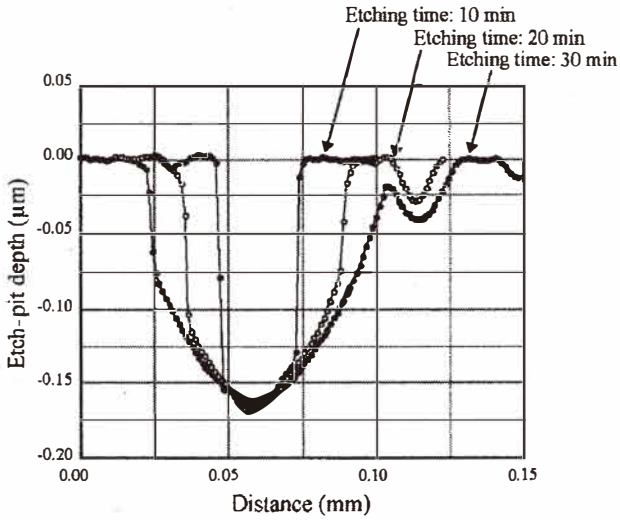

Fig. 4. Change in etch pit cross section after saturation in etch depth, that was observed on a wafer not subjected to oxidization prior to etching in 40%KOH at 70°C.

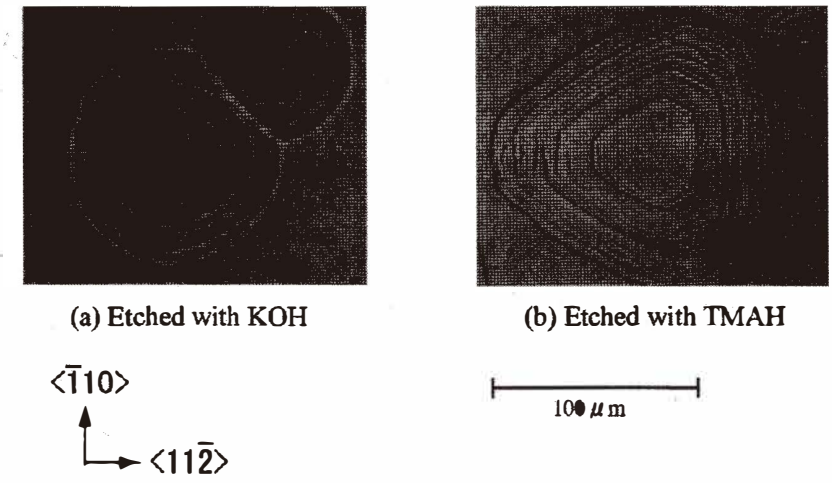

Fig. 5. Comparison of the etch-pit profiles between (a) KOH and (b) TMAH etching.

3.2 *Difference in activated atomic steps*

When (111) was etched with two different solutions, KOH and TMAH, top views of etch-pits were quite different between the two etchants. The top views of the etch-pits are compared in relation to the crystal orientation in Figs. 5(a) and (b), respectively. Both etch-

pits (a) and (b) are triangular rather than hexagonal. However, the vertexes of the triangle are directed oppositely in terms of crystal orientation. This can be confirmed by (a) and (b). It is observed that the left-hand sidewalls are steeper than the right-hand ones when etched with KOH. On the contrary, the right-hand sidewalls are steeper than the left-hand ones when etched with TMAH. It is clear that the ratio of the sidewall steepness, i.e., the ratio of the lateral movement velocity of the two different types of steps aligned to $[11\bar{2}]$ and $[\bar{1}\,\bar{1}2]$, was reversed between KOH and TMAH.

3.3 *Correlation between nano- and macroscopic anisotropy*

Our experimental results can explain the macroscopic etching behavior of silicon in the vicinity of (111) that is etched by KOH or TMAH solution.

We previously measured the etching rate of silicon as a function of crystallographic orientation, and found a significant difference in anisotropy between the two etchants.[6] Figure 6 compares the macroscopic anisotropy of single-crystal silicon etched with KOH and TMAH in terms of contour maps of the etching rate. Though the etching rate minimum was located at (111) orientation for both etchants, the triangular contour patterns in the vicinity of (111) rotate by 60 degrees between the two etchants.

This is well explained by our observed results showing that the ratio of step velocities aligned to $[11\bar{2}]$ and $[\bar{1}\,\bar{1}2]$was reversed between KOH and TMAH.

The edge of the three-backbonded step is more stable than that of the two-backbonded step in case of KOH etching. However, in case of TMAH, two-backbonded steps are more stable than three-backbonded ones.

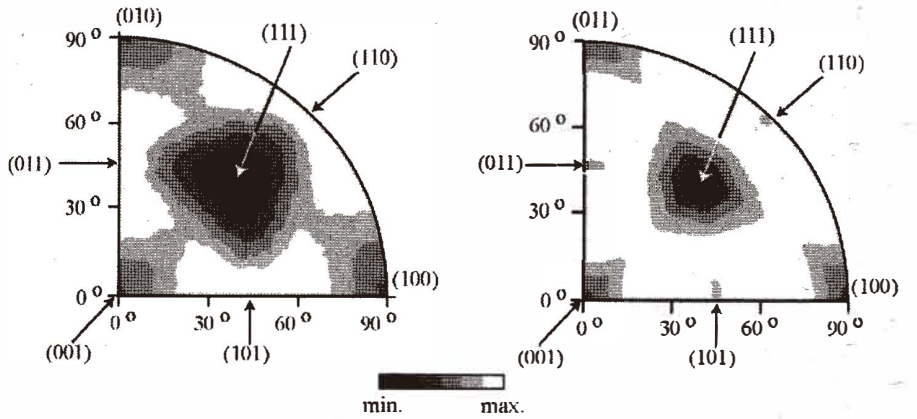

Fig. 6. Comparison of macroscopic anisotropy in etch-rate contour map between (a) KOH and (b) TMAH etching.

4. Conclusion

The following findings explain the differences in macroscopic etching behavior between KOH and TMAH water solutions.

(1) Etching of (111) silicon surface substantially advanced as a result of lateral movement of steps of 20–50 nm in height.

(2) Defects on the (111) surface are one type of seed of such steps. The defects can be introduced by thermal oxidation of the wafer.

(3) The linear steps on the (111) surface are classified into two groups which are perpendicular to $[11\bar{2}]$ and $[\bar{1}\,\bar{1}\,2]$, respectively, and result in hexagonal etch-pits on (111) surface.

(4) The three-backbonded step edge on the (111) surface becomes more active than the two-backbonded one in case of TMAH etching, opposite to the case of KOH etching.

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