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LETTER

New Observations on Pyramidal Hillocks in the Anisotropic Etching of <100> Silicon

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In the anisotropic etching of crystalline <100> silicon, pyramidal hillocks with square bases and <111> planes forming the pyramidal surfaces have often been observed and reported. Our previous observations showed that these pyramids appear and then disappear on the <100> etch plane. We present an explanation for the appearance of the pyramids and describe the mechanism of their disappearance, which is significantly different from that proposed earlier. A video has been produced which shows the process of anisotropic etching of <100> silicon *in situ*, as well as the appearance and disappearance of the pyramids on the etch plane.

1. Introduction

The anisotropic etching of silicon (micromachining) has become a crucial process step in the production of microsensors, microactuators and other novel devices. During the etching process, the appearance of pyramidal hillocks (see Fig. 1) has been observed and reported. The presence of these pyramids is undesirable as they can have adverse effects on the mechanical or electrical characteristics of microstructures due to the increased surface roughness. For example, in diaphragm-based microsensors, depending on the thickness of the diaphragm, the pyramids can affect the stress distribution, and hence the mechanical integrity. In silicon field emitter arrays, the pyramids can perturb the electric field

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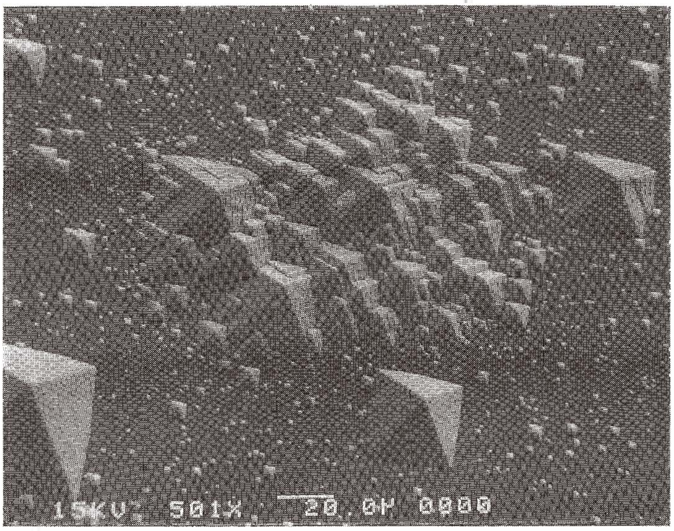

Fig. 1. SEM micrograph of anisotropically etched <100> silicon surface showing the presence of pyramidal hillocks.

distribution and possibly the emission characteristics. Therefore, it is important to develop a better understanding of the origin and, if possible, the elimination of these pyramids. A number of previous reports have suggested that using an appropriate concentration of the etchants can result in pyramid-free surfaces, but the results have not always been consistent and caution is necessary, as noted below, before this finding can be generally accepted.

In a previous report we[1] described in detail some of the peculiar features of the pyramids observed during the anisotropic etching of <100> silicon using an ethylenediamine-pyrocatechol (EDP) solution. We suggested that the pyramids appear due to the incomplete removal of the hydrated oxide by the etchant as well as the presence of structural and/or compositional defects in the bulk of the silicon substrate. Micrographic evidence indicating that the location of the pyramids on the etch plane was strongly affected by the thermal and stress history of the substrate wafer was presented. We reported the first observations on the disappearance of the pyramids from the etch plane and we also proposed a mechanism for this process.

2. Materials and Method

In this work, we report our *in situ* observations of the anisotropic etching of <100> silicon using EDP, which have been recorded on video. The proposed mechanisms are re-examined in light of these new observations. Figure 2 shows a schematic of the observation apparatus. The maximum magnification of the microscope was about 500. The

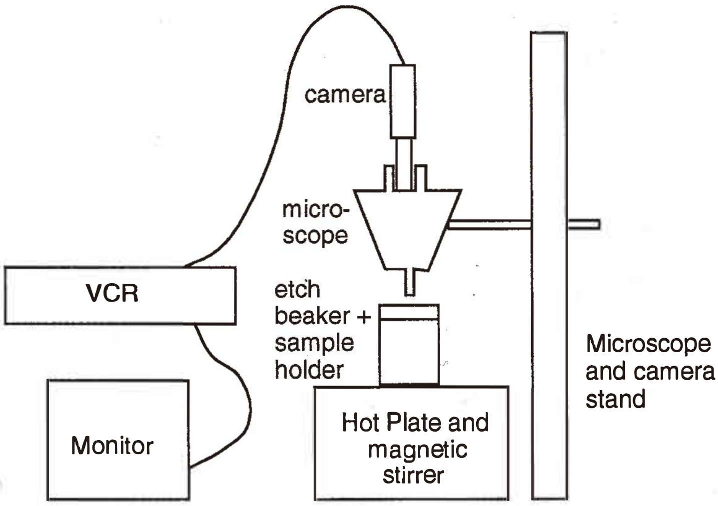

Fig. 2. A schematic of the *in-situ* etching observation apparatus.

charge-coupled-device camera was connected to the color monitor via the video cassette recorder, so that video recordings could be made of any period of the *in situ* observations. The EDP solution was made with 216 gm of pyrocatechol dissolved in 475 ml of deionized water and 1 litre of ethylenediamine. The mixture was heated to between 90 and 95°C on a temperature-controlled hot plate and gently stirred using a magnetic stirrer. The experiments were performed with freshly prepared EDP in an 800 ml beaker containing about 790 ml of the etchant solution. The 3" diameter c-Si wafers were oxidized to form an oxide layer 1 μm thick and patterned to expose less than 10% of the top silicon surface, leaving the oxide layer on the back of the wafer intact.

3. Results and Discussion

Firstly, in recent studies[2–4] the distribution of oxygen precipitates in silicon wafer substrates has been measured. The results have shown that in well-gettered silicon wafers, the concentration of oxygen in the superficial silicon regions is actually very low and that most of the oxygen is successfully driven into the bulk of the wafer. It is interesting to note that we have not observed the appearance of pyramids in approximately the first ten microns of the wafer, nor are we aware of any studies in which this observation has been made. Secondly, our observations show clearly that the surface density of the pyramids on the etch plane increases as the etch depth increases. In most of the reports in which it is suggested that an appropriate concentration of the etching solution can be employed to remove the pyramids, the micrographs of the etched planes shown for various concentrations of the etchant do not exhibit the same etched depth. Since the silicon etch rate is strongly dependent on the concentration of the etchant, the etched depth is significantly smaller for the cases purported to be "pyramid-free" because of the different concentrations of the etchant. If the appearance of the pyramids on a silicon wafer free from local stress variations is caused by bulk oxygen "defects" which the evidence mentioned above leads us to believe, then these previous observations of pyramid-free surfaces are inconclusive unless they are made on etch planes at very similar etched depths. Our observations lead us to believe strongly that the appearance of the pyramids on the etch plane is caused by the bulk oxygen compositional defects appearing on that surface.

The theory that the pyramids are caused by bulk oxygen defects is also supported by consideration of the etch rate kinetics. As is well known, the anisotropic etching of silicon progresses via oxidation and chelation reactions. Thus, the maximum silicon etch rate occurs at an etchant concentration at which the rates of oxidation and chelation are optimized simultaneously. In the case of aqueous EDP, the ethylenediamine + water combination is the oxidizing agent, and pyrocatechol functions as the chelating agent.[5] If the relative concentrations of these constituents are changed, the slower of the two reactions determines the net silicon etch rate. Similarly, using an etchant consisting of potassium hydroxide (KOH), tetra-methyl ammonium hydroxide (TMAH), ammonium hydroxide water (AHW) or hydrazine it has been shown that increasing the concentration of these reagents can lead to pyramid-free surfaces on silicon. Assuming that the observations were made at depths greater than about 10 μm from the polished surface of the substrate wafer, the absence of the pyramids can be explained simply by arguing that changes in the etchant composition enhanced the chelation reaction and subdued the oxidation reaction, thus preventing the bulk oxygen precipitates from forming pyramids. In separate experiments, we have observed that adding pyrazine to the EDP solution also inhibits the formation of the pyramids, and it is known that pyrazine enhances the oxide etch rate. Finally, it has been reported[6] that the pyramids are most likely to appear at the etchant composition which gives the highest silicon etch rate, which appears to be contradictory to our understanding that at this etchant concentration the chelation rate must be optimized. However, at this particular etchant concentration the silicon oxidation rate is also maximized, and if the two optimized rates are different (the silicon oxidation rate being higher), then it is likely that the pyramids will be formed due to oxygen defects in the bulk.

As for the disappearance of the pyramids from the etch plane, we previously proposed that the three-dimensional convex corner at the tip of the pyramid etches away extremely rapidly after the etch-resistant structure at the pyramidal tip is completely etched. In fact, our new *in situ* observations show conclusively that the pyramids are etched away from one of the corners of the base, as can be seen in Fig. 3. However, this process is quite rapid. A pyramid which has withstood, for example, one hour of etching by EDP can disappear completely within about one minute after one of the corners on the base of the pyramid becomes rounded. Typically, one of the corners of the pyramid on the etch plane becomes rounded, followed by the other corners, which can lead to the formation of complex shapes (Figs. 4(a) and 4(b)) before the pyramid disappears completely, leaving behind a flat <100> surface. It is not clear why the disappearing pyramids have very odd and yet

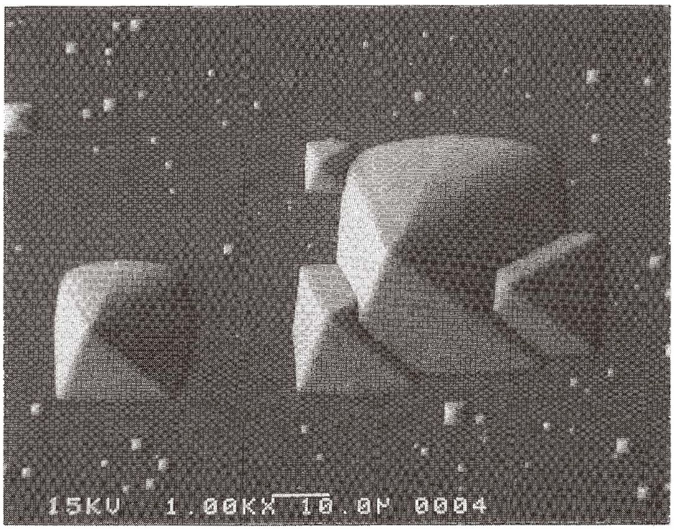

Fig. 3. SEM micrograph showing two pyramids, with rounded corners, at the beginning of the process of being etched away completely.

somewhat regular (transient) shapes, which consistently appear to be at a specific angle (Fig. 4(b)) to the original pyramid.

4. Conclusions

We have presented experimental observations on the formation and disappearance of pyramidal hillocks on the etch plane of <100> silicon. We have correlated these observations with those in other reports, which, when taken together, suggest strongly that the pyramids are formed because of the presence of residual oxygen defects in the bulk silicon. A study of oxygen implanted silicon wafers is underway in an attempt to confirm these results.

(a)

(b)

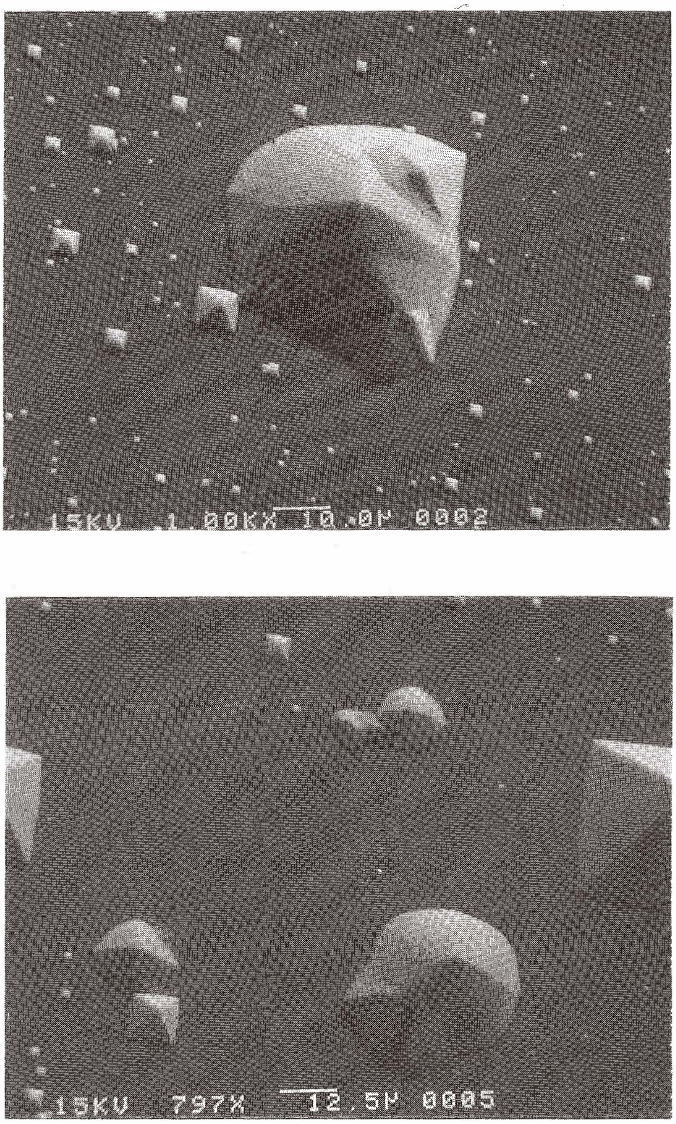

Fig. 4. SEM micrographs showing a few of the complex transient shapes which the disappearing pyramids exhibit during the etching process.

References

1 Y. K. Bhatnagar and A. Nathan: Sensors and Actuators **A 36** (1993) 233.
2 D. Guidotti, M. A. Taubenblatt, S. J. Batchelder, R. L. Kleinhenz and A. A. Dupnock: Appl. Phys. **A 55** (1992) 139.
3 K. Sueoka, N. Ikeda and T. Yamamoto: Appl. Phys. Lett. **65** (1994) 1686.
4 S. Kimura: J. Electrochem. Soc. **141** (1994) L120.
5 A. Reisman, M. Berkenbilt, S. A. Chan, F. B. Kaufman and D. C. Green: J. Electrochem. Soc. **126** (1979) 1406.
6 J. Greenwood: J. Phys. E: Sci. Instrum. **21** (1988) 1114.