Absolute etch rates in alkaline etching of silicon (1 1 1)

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ABSTRACT

The absolute etch rate of silicon (1 1 1) during wet chemical etching in aqueous KOH solution has been investigated with optical interferometry, using masked samples. The etch rate is constant at $0.62 \pm 0.07 \,\mu m/h$ and independent of alkaline concentration for 1–5 M KOH solutions at 60 °C. Only at lower alkaline concentrations, the etch rate decreases. Adding isopropanol slightly lowers the absolute etch rate. The activation energy of the etching reaction is 0.61 ± 0.03 eV in standard KOH solutions and 0.62 ± 0.03 eV with 1 M isopropanol added to the solution. This indicates that the reaction is determined by reaction kinetics and not by transport limitations. In all cases the surfaces are covered by shallow etch pits, not related to defects in the crystal. This implies that the actual factor that determines the etch rate is the 2D nucleation of new vacancy islands at the bottom of these pits. This process is likely catalyzed by a local accumulation of reaction products, which preferentially occurs near the mask edges.

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1. Introduction

Anisotropic wet chemical etching of silicon is an extensively used process and an essential step in micro-electromechanical systems (MEMS) manufacturing [1–5]. The process is based on the significant difference in etch rate between the {1 0 0} and {1 1 0} faces versus the {1 1 1} faces of the silicon crystal [6–9]. As the Si-{1 1 1} plane is the slowest etching plane in KOH solution [10–14], wet chemical anisotropic etching is normally applied to masked (1 1 0) and (1 0 0) wafers, resulting in complex three-dimensional structures bounded by {1 1 1} planes. The difference in etch rate between the slowest {1 1 1} faces and the other two crystallographic orientations of silicon during etching is also known as the anisotropy ratio, which is a major factor in determining MEMS quality. In contrast to the fast etching (1 0 0) and (1 1 0) planes, knowledge of the absolute etch rates of "exactly" oriented (1 1 1) faces is still lacking. In addition to the processing of (1 0 0) and (1 1 0) Si wafers, knowledge of Si-{1 1 1} etching is also important for the processing of (1 1 1) oriented wafers as a route to obtain smooth surfaces and different kinds of free-standing microstructures [10,15–17].

A second aspect of the wet chemical etching of Si-(1 1 1) using alkaline etchants is its mechanism, which totally differs from that of the other silicon crystal orientations. Whereas the KOH etching of the other, either exact or vicinal, Si-faces $(h\,k\,l)$ involves step flow, step bunching, pyramid formation or kinetic roughening [18], the etching of the exact {1 1 1} plane proceeds by a repeated 2D nucleation of vacancy islands, which then expand by step flow, leading to the development of shallow, point bottomed etch pits [19,20]. Such a process of step generation can be induced by the stress fields around dislocations or stacking faults ending on the (1 1 1) face [21,22], but in our study the pits are not related to defects and the 2D nucleation of steps is likely induced by a local accumulation of silicate reaction products [19,20]. However, quantitative data on the kinetics of this etching process is not yet available.

Methods based on the etching of wagon wheel patterns [11,23–25] or of semiconductor (hemi)spheres [18,26] have the advantage of yielding dissolution rates for a whole range of orientations in a single experiment. Unfortunately, these otherwise powerful approaches do not provide information on the etch rate of the exact {1 1 1} face, as this is readily etched away and replaced by vicinal faces close to {1 1 1}. This follows from the kinematic wave theory of crystal dissolution, according to which the slowest etching face on a curved surface will disappear during etching [27]. Examination of cleaved silicon samples with etch structures bounded by {1 1 1} faces, using optical microscopy or scanning electron microscopy (SEM), can provide information on absolute etch rates of {1 1 1} surfaces. However, this approach is quite tedious and the etch rate might be affected by the presence of the mask contacting the {1 1 1} faces. Another experimentally very challenging way of determining the etch rates is by using in situ STM observation of the Si-(1 1 1) surfaces during etching [28]. Although this method provides detailed information on the etching process at a nanometer scale, the measured etch rates are not representative for the larger scales used in MEMS technology. Moreover, this method can only be used for relatively low alkaline concentrations. From

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the above it is clear that, although measuring absolute etch rates of Si-{1 1 1} accurately is highly relevant in MEMS technology, it has been proven not to be a trivial exercise.

A large number of studies have been carried out on the etch rate and surface morphology of the {1 0 0}, {1 1 0} and other {h k l} faces of silicon etched in alkaline solutions, with and without additives, e.g. see Refs. [29–31]. However, the {1 1 1} faces received less attention, as the commonly used methods for the measurement of etch rates are not suited for the slowly etching {1 1 1} faces.

In this study we determine accurate {1 1 1} etch rates by etching partially masked Si-{1 1 1} wafers followed by measurement of the resulting height differences between the masked and free surface areas using phase shifting interferometry (PSI). By this straightforward approach the problems encountered by the methods mentioned above are avoided. The absolute etch rates are measured with and without isopropanol (IPA) additive and as a function of time, the diameter of the non-masked areas, KOH concentration and temperature. The activation energy of the wet chemical etch reaction is determined from the temperature series. Complementary to the etch rate measurements, the morphology of the etched surfaces is inspected using PSI and differential interference contrast microscopy (DICM). These morphologic observations provide important information on the influence of mask edges on the surface profile and the measured etch rates.

2. Experimental procedures

2.1. Sample preparation

All samples were prepared from Czochralski grown, 4-in. (1 1 1)-oriented p-type silicon wafers supplied by Okmetic (boron doped, resistivity 5–10 Ω cm, diameter 100 ± 0.5 mm, thickness 525 ± 25 μm, misorientation <0.5°). The sample wafers were masked by LPCVD deposition of a 300 nm thick (low stress) silicon-rich nitride (SiRN) layer. Conditions: 9200 mTorr, 850 $^\circ$C, 70 sccm SiH_2Cl_2, 18 sccm NH_3. To obtain oriented arrays of circular openings, one lithography step was used after wafer alignment along the wafer flat. This alignment facilitates determination of the crystallographic orientation of the surface patterns after etching. The circular areas in the nitride layer were opened by a plasma etch (Dry Reactive Ion Etching (DRIE)) followed by a short fluoride etch (48% HF) and removal of the photoresist. The mask obtained in this way consists of a pattern of circular openings with diameters 0.5, 1, 2 and 5 mm. The masked samples were diced into samples of 20.0×20.0 mm^2.

Prior to the etching experiments, the samples were cleaned in Piranha acid (98% H_2SO_4:35% H_2O_2; 3:1) for 10 min to remove organic deposits and then immersed in ultra pure water for 15 min. The final nitride removal in the mask openings was done using 48% HF, followed by a thorough rinse in ultra pure water ($\rho \sim 15$ MΩ cm). After cleaning, etching was carried out by placing the diced samples in a Teflon beaker, containing 200 ml of aqueous KOH solution, which was sealed with parafilm to avoid evaporation. Standard aqueous KOH (Merck, p.a.) solutions were used of 2.0 M and 5.0 M concentration, by dissolving the KOH pellets in ultra pure water. In one part of the experiments, the standard solution was used, in the remaining experiments IPA (Merck, selectipur VSLI) was added to the solution at a concentration of 6.5 wt% relative to water (equal to about 1 M IPA). To investigate the time behavior of etching, the samples were etched for time intervals of 2 h up to 20 h at 60 $^\circ$C in duplo by placing the beakers in a thermostatic bath with an accuracy of 0.1 $^\circ$C. Prior to microscopic examination, the etching process was quenched by immersing the sample in diluted sulfuric acid (10%) for at least 10 min. After this, the spec-
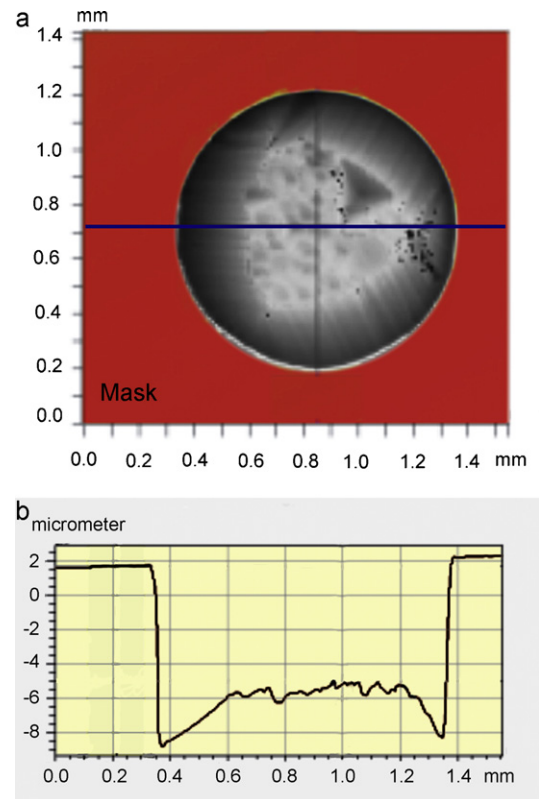
Fig. 1. Determination of the vertical etch depth by using white light phase shifting interferometry. A circular opening of 1 mm is measured to accurately determine the depth profile of the etched silicon. (A) Overall image showing the depth distribution represented as a variation in gray level. (B) Depth profile along the horizontal line in (A). The crystal was etched for 8 hrs in a 5 M KOH solution with 1 M IPA added at $T = 60$ $^\circ$C.

imens were rinsed in ultra pure water and blown dry in a flow of argon.

2.2. Sample analysis

The etch rates were derived from the measured height differences between the masked and etched surface areas of the specimen crystals. The measurements were carried out using white light PSI (Wyko NT1100), a method capable of gauging height differences ranging from a few tens of micrometers down to nanometers. In interpreting the measurements a correction is made for the 300 nm thick masking layer. Fig. 1 shows a top view and a depth profile of a circular mask opening after etching, as obtained by PSI. By choosing longer etching times, the influence of the slight misorientation of the non-masked surface areas with respect to the exact (1 1 1) plane can be ignored, as prolonged etching will overcome this effect because the etch pits formed with slopes of about 0.5° are steeper than this misorientation. The etch depths (rates) given in Figs. 2–5 were measured at the centre of the circular mask openings. Each point in these graphs represents the average value of the etch depth of minimal three different mask openings of identical size. The surface morphology of the samples was examined using DICM, by which method the shallow slopes of the step and pit patterns can readily be imaged. This is different from using scanning electron microscopy (SEM), which is the standard method for imaging MEMS structures. By application of this technique, which allows for higher magnifications, the shallow pit inclinations on the etched surfaces could hardly or not be imaged. Therefore, we were not able to obtain morphologic information on the narrow {1 1 1} side walls bounding the etched mask openings.