

Detection of Discontinuities in Passivating Layers on Silicon by NaOH Anisotropic Etch

Abstract: Discontinuities in glasses deposited on silicon substrates are readily detected by a silicon-preferential etch that uses single component alkali solutions. The etchants can be applied to thermally grown oxide films, pyrolytically-deposited passivating layers or sputtered quartz. The character of the discontinuities in these films is shown and the size can be estimated (although both observations are subject to the limitations of the optical tools used for observation or micrography). When applied in the temperature range below +70°C, the etchant attacks the oxides insignificantly and the concentration, as well as the temperature, is chosen for convenience. Above +70°C the passivating layers, particularly thermal SiO₂, are etched at higher rates, and the etching effects must be taken into account if the oxide thickness is less than 1000 Å. The etchants are applicable to intrinsic as well as extrinsic silicon up to a doping level of 10²⁰ cm⁻³.

Introduction

The term "pinhole" embraces a wide variety of oxide defects and is used today in a broad sense [1]. Listed in this category are cracks caused by thermal contraction after oxidation or by handling, and regions of oxide with low dielectric strength caused by dust particles, inadequate masking, contamination, or poor photoresist adhesion [2,3]. Each of these factors, however, causes the oxide defects to be different in appearance, size or electrical properties. Knowledge of the characteristics of the several types of defects allows them to be classified and provides some information about their various causes. Techniques are desirable that 1) distinguish among classes of defects (e.g., discontinuities as compared with dielectrically weak spots) and 2) reveal the specific nature of varieties within a class (e.g., the geometry of a discontinuity that identifies its crystallographic orientation).

Several pinhole detection techniques have been developed in recent years. Some of them are based on chemical etching of the silicon in the regions of oxide discontinuity; others are based on electrolysis. To the first group belong chlorine etching [4], catechol-hydrazine etching [5], and etching based on a ternary mixture of water, ethylene-diamine and pyrocatechol [6]. The second group comprises plating, decoration and gas evolution techniques.

Etching techniques sometimes have the disadvantages [5,6] of being lengthy and tedious, e.g., ethylenediamine etching [6], or of creating hostile emissions requiring safety equipment, e.g., chlorine etching [4], but they have the advantage of better discrimination among the types of defects they reveal. For example, in one comparison [7] Goldstein and Spencer applied the gas evolution technique and correlated the results with those from the catechol etch. The number of pinholes found by evolution, averaged over 10 wafers, was four times higher than the result of the catechol etch. The reason for the difference seems to be that the catechol etch shows physical openings only, whereas gas evolution and frit decoration indicate all leakage paths. Because the voltage applied using the latter techniques is relatively high (ranging from 40 to 100 volts), thin oxide areas are also shown as pinholes. The fact that etching techniques generally do not show dielectrically weak spots makes them preferable for investigating oxide discontinuities, i.e., physical openings, provided that the etching rates for SiO₂ are very low compared with those for silicon. It is desirable, however, to find an etchant that is relatively easy to use while still providing the necessary results.

Under the proper conditions solutions such as NaOH in water are found quite suitable. They eliminate most of

Table 1 Comparison of etchants applied to oxide discontinuities.

<i>Etching technique</i>	<i>Etching temperature (°C)</i>	<i>Applicability</i>	<i>Etching time (min)</i>	<i>Remarks</i>
Chlorine gas [4]	≈ 910	Elemental and doped silicon	16	Toxic; high temperature
Pyrocatechol ethylene-diamine with alcohol [6]	110	Elemental silicon only	360	Complex preparation; limited to intrinsic silicon; time for preparation not included.
Catechol-hydrazine, aqueous or anhydrous [5]	100	Elemental and doped silicon $\leq 10^{18} \text{ cm}^{-3}$	≥ 15 For nominal size of about $2.5 \mu\text{m}$; depends on crystal orientation and doping level	Data obtained from [5], based on the rate of silicon removal.
Hydroxides of alkali metals in aqueous solutions (LiOH, KOH, NaOH)	≤ 70	Elemental and doped silicon $\leq 3 \times 10^{20} \text{ cm}^{-3}$	≥ 3 Depends on size of discontinuity and type of silicon	Applicable to both types of doped silicon. Above $3 \times 10^{20} \text{ cm}^{-3}$ of p-type dopant, reaction is hardly noticeable within the usual time of etching.

the mentioned disadvantages and are characterized in the following way:

1. The technique is simple; no specific sample preparation is necessary.
2. The time for processing is short; runs can be completed in 5 to 10 minutes once the temperature and etchant concentration have been selected.
3. The technique is relatively safe; a temperature below 70°C and concentrations as low as 0.05 mole per liter yield quite satisfactory results.

Table 1 lists a comparison among known etching techniques. It is evident from the table that the alkali single-component solutions are not only more convenient because of lower temperature and shorter processing time, but that they also have the ability to etch more heavily doped silicon ($> 10^{18} \text{ cm}^{-3}$), a property that pyrocatechol and catechol-hydrazine etches lack.

Experimental

Czochralski-grown silicon wafers of three basic low index orientations were used throughout the experiments. The wafers represent intrinsic as well as extrinsic silicon doped with P, As and B. A number of wafers were processed through dry oxidation at 1000°C in an oxygen atmosphere, while steam oxidation at 1150°C was used for several others. The thickness of thermal oxide ranged from $\approx 120 \text{ \AA}$ to about $5400 \text{ \AA}$. Samples with pyrolytic oxide and sputtered SiO_2 were included in the experiments. The thicknesses of these latter oxides were $1.5 \mu\text{m}$ and $2400 \text{ \AA}$ respectively. The usual etchant applied was 10 grams of NaOH dissolved in 100 ml of

deionized (DI) water, but KOH and LiOH etchants were found to perform in a similar manner, as would be expected.

• Detection of pinholes in SiO_2

A glass dish containing not less than 100 ml of etchant was placed in a water bath at $65 \pm 5^\circ\text{C}$. Since the effect of concentration above 2 percent wt. on the etching rate is rather small, the concentration was arbitrarily chosen at about 10 percent wt. Neither the concentration nor the temperature in the range below 70°C was critical.

Samples were mounted on a glass slide by using black wax in such a manner that the backside of a wafer faced the glass and the oxidized side was exposed to the etchant. Samples were rinsed in DI water prior to immersion. After the desired temperature was reached, the samples were immersed into the solution. For n-type, intrinsic and p-type doped substrates up to $\approx 10^{19} \text{ cm}^{-3}$, 3 to 10 minutes immersion was enough. For a heavily doped p-type a longer time was needed. For example, with a doping level of $3 \times 10^{20} \text{ cm}^{-3}$ about 45 minutes or more were necessary. It appears that in this reaction electrons rather than holes are required.

The temperature of 65°C chosen here is high enough to accelerate the etching process substantially, and remains sufficiently low not to create experimental difficulties such as etching of SiO_2 .

After etching the sample was rinsed in a stream of water and dried by an air blower.

After preparation in this manner, the material was ready for visual inspection, pinhole count, or micrography. Throughout the experiments a C. Zeiss Ultraphot

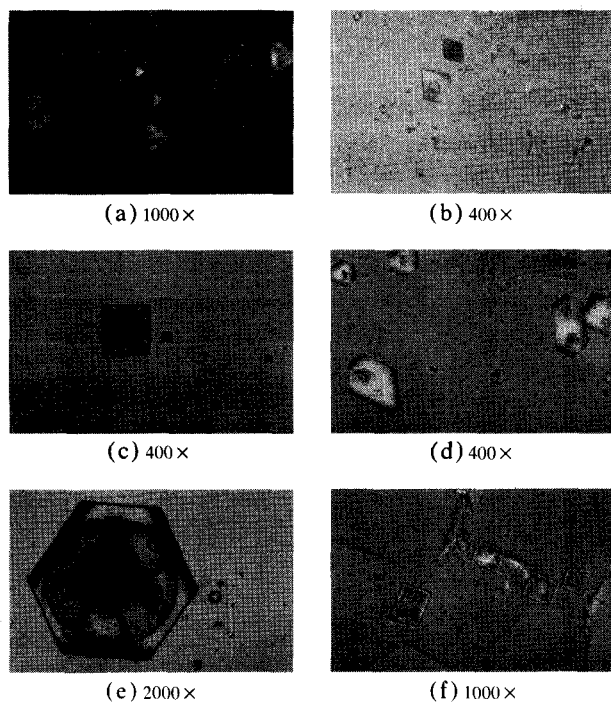


Figure 1 Characteristic geometry of etch pits around discontinuities as seen through the oxide layer: (a) Thermal SiO_2 over a $\langle 111 \rangle$ oriented p-type substrate; (b) thermal SiO_2 over a $\langle 110 \rangle$ oriented intrinsic substrate; (c) thermal SiO_2 over a $\langle 100 \rangle$ oriented epitaxially grown n-type substrate; (d) sputtered SiO_2 over a $\langle 111 \rangle$ oriented p-type substrate; (e) pyrolytic SiO_2 deposited by $\text{SiCl}_4 + \text{O}_2$ at 475°C over a $\langle 111 \rangle$ oriented intrinsic substrate; (f) thermal SiO_2 over a $\langle 100 \rangle$ oriented p-type substrate distorted by mechanical working prior to oxidation. (Original magnification is shown beneath the photographs; in this and subsequent Figures the actual size varies from the original due to reduction for publication.)

II Metallograph was used. Observations were made at a minimum of $200\times$ magnification, and the micrographs were taken at a magnification not lower than $400\times$. Figure 1 shows characteristic geometrical symmetries of etch pits in the silicon for different substrate orientations, substrate types and various kinds of passivating layers, as viewed from the side of the inspected oxide. The polygons observed are the etch pits in silicon in the areas where openings in the oxide exist.

• Determination of the nature of a discontinuity

Anisotropic etching properties of NaOH are similar to those of other known etchants for silicon in the sense that they do preferentially expose the $\{111\}$ planes. Because of this preference, continued etching will proceed inward, away from the edges of the oxide discontinuity and into the bulk silicon in the directions parallel to the surface, as well as downward along the $\{111\}$ planes. This process enlarges the etch pits but preserves their characteristic geometry and leaves intact the un-

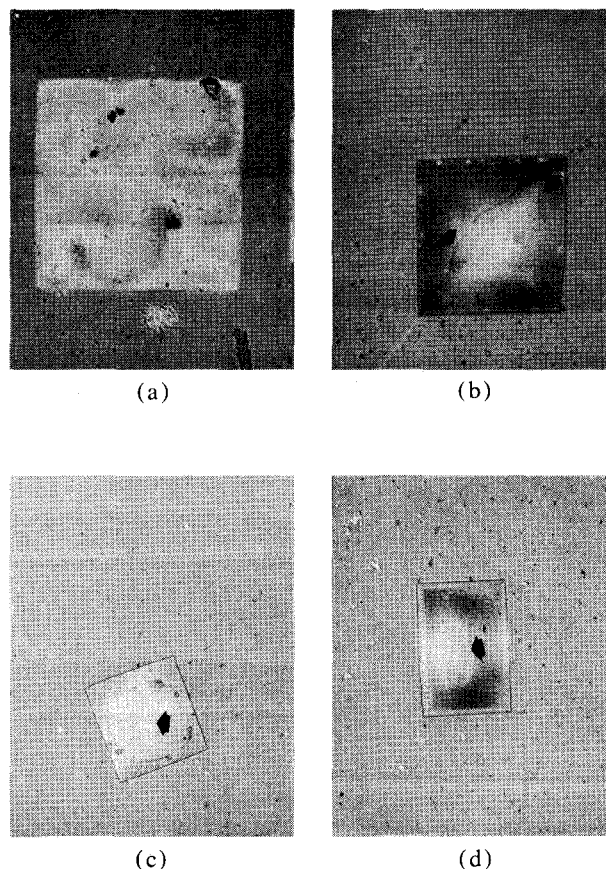


Figure 2 Thermal oxide discontinuities, revealed through NaOH etching, in a $\langle 100 \rangle$ oriented n-type substrate (original magnification $1000\times$): (a) Region of porous oxide; (b) crack in thermal oxide resulting from a scratch; (c) a submicron pinhole; (d) large area of missing oxide (oxide thickness $\approx 1400 \text{ \AA}$).

damaged oxide above the enlarged pits. The etching is done in a manner similar to etching for pinholes. In this case, however, damage to the oxide must be avoided, and therefore no agitation is applied and the rinsing is accomplished by soaking the sample in a large amount of water. The sample is placed in a vessel filled with about 250 ml of DI water for at least one-half hour and then left to dry. For determination of the size and shape of a discontinuity (hole, crack) a magnification of at least $1000\times$ is needed. Figures 2, 3 and 4 illustrate the character of various discontinuities in SiO_2 . Figure 2 (a) shows a porous SiO_2 where neither the size nor the exact location of holes is determined at this magnification. In all other cases the shape and size are clearly defined.

• Affinity of ROH etch to the oxide discontinuities

An oxidized $\langle 100 \rangle$ oriented wafer with an n-type epitaxial layer was processed through the photoresist masking to create a geometrical pattern in SiO_2 for subsequent boron diffusion into Si. The wafer was etched for

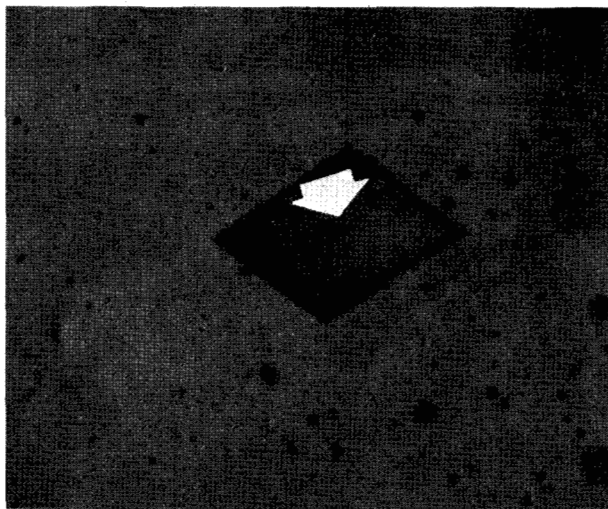
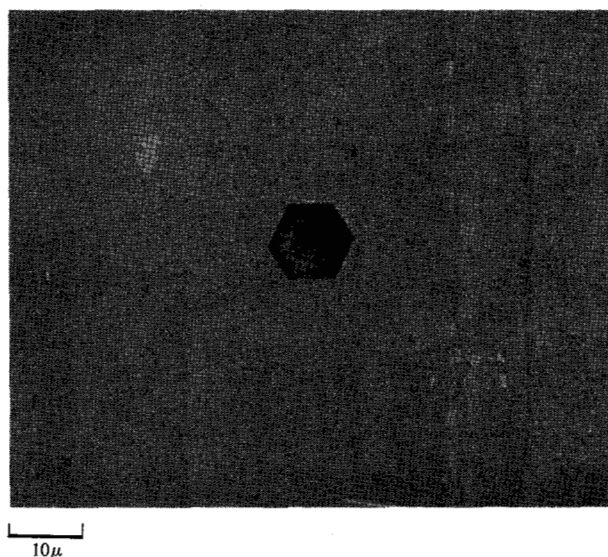


Figure 3 A single crack in the oxide on a $\langle 110 \rangle$ oriented intrinsic substrate, probably stress induced. Direction of the crack is $\langle 100 \rangle$ (oxide thickness $\approx 4000 \text{ \AA}$; original magnification $2000\times$).

Figure 4 Circular opening in the oxide on a $\langle 111 \rangle$ oriented n-type epitaxial substrate, presumably a photoresist defect (oxide thickness $\approx 3500 \text{ \AA}$; original magnification $1000\times$).



10 minutes in NaOH, inspected, and the locations of orthogonal etch pits were mapped and counted at $400\times$. Figure 5(a) shows an example of the pattern and a group of etch pits resulting from inadequate masking. This wafer was subjected to boron doping of the exposed silicon at a surface concentration in excess of $3 \times 10^{20} \text{ cm}^{-3}$.

If the etch pits are associated not only with physical openings but also with thin oxide or intrusions of foreign matter into the SiO_2 , all the sites of p-type material

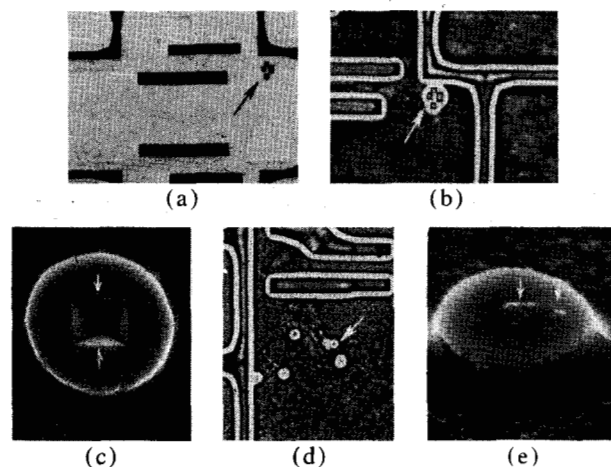


Figure 5 Difference between holes in the oxide and the embedment of foreign matter in SiO_2 as shown by etching in ROH: (a) A group of openings in SiO_2 exposed by etching (arrow) concurrently with etched pattern prepared for boron diffusion (dark areas) in n-type silicon (original magnification $400\times$); (b) same pattern after boron diffusion, oxide stripping and selective etching of n-type material. The bright regions are the p-type areas with boron concentration of about $3 \times 10^{20} \text{ cm}^{-3}$ ($400\times$); (c) an isolated p-type island with characteristic crater (arrows) created by ROH etching prior to diffusion due to the presence of a discontinuity in SiO_2 (SEM, originally $4000\times$); (d) a group of parasitic p-type islands resulting from embedment of foreign matter in SiO_2 . Absence of craters indicates no openings were present prior to diffusion (arrow); (e) a single p-type island with foreign matter on the surface indicated by arrows (SEM, originally $4000\times$).

should be marked by characteristic pits, further referred to as craters. These p-type islands can be exposed by either staining or selective etching for different types of silicon. In the experiment the wafer was stripped of SiO_2 in concentrated HF, and the n-type material was removed by selective etching, leaving p-type silicon exposed in the form of mounds. Figures 5(b) and (d) exemplify a sample processed through selective etching. It is observed that some of the p-type mounds lack the characteristic crater, as shown in Fig. 5(c). The counts taken prior to diffusion and after selective etching revealed 363 craters in both cases, while the total number of p-type mounds was 409. On those mounds that had no craters, some material is observed [Figs. 5(d) and (e)]. This material was not identified but, because it was not etched by the HF, it certainly was not SiO_2 . Moreover, the absence of craters indicates that this matter was an effective barrier to NaOH etch but at the same time allowed boron diffusion. The conclusion is that ROH etch does not expose embedments of foreign particles as pinholes in SiO_2 .

To determine whether or not the ROH etch exposed dielectrically weak spots due to very thin passivation, a silicon wafer was oxidized for a very short time, and ellipsometric measurement showed an oxide thickness of

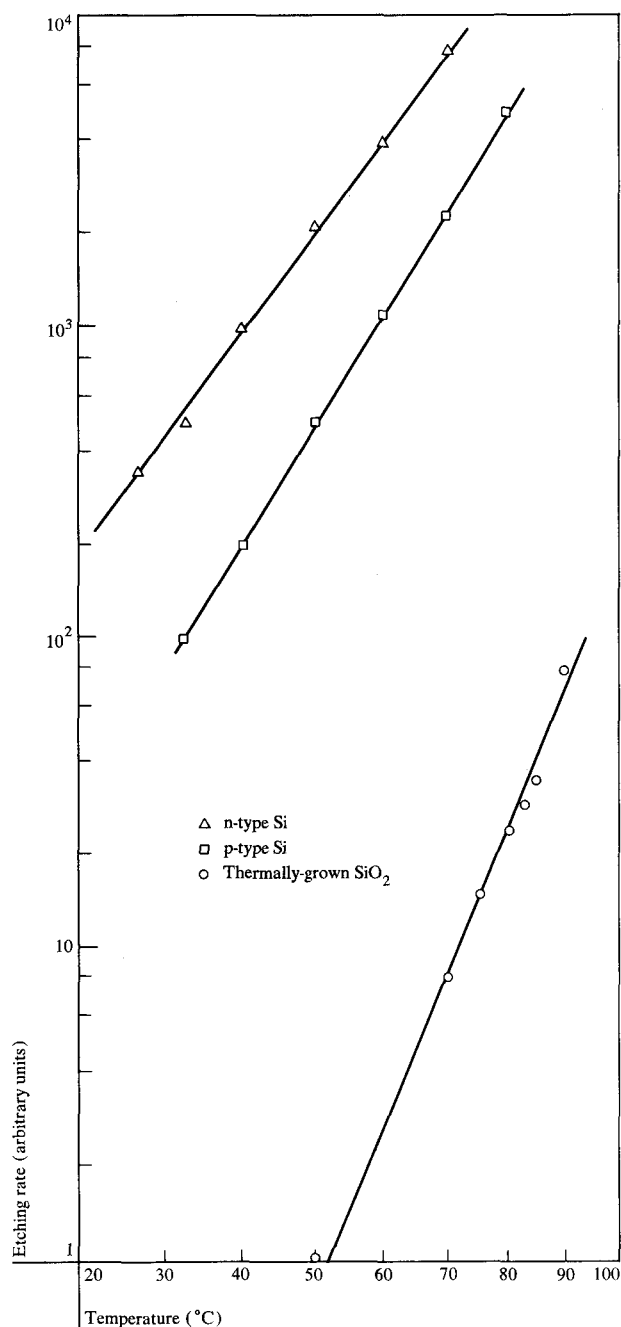


Figure 6 Etching characteristics for n-type and p-type silicon and thermally-grown SiO₂; etchant is NaOH.

124 Å. This wafer was divided into two parts; one part was stripped of passivation and the other was left with the oxide. Both samples were etched concurrently at 65°C for 15 minutes. On the surface of the sample without passivation, evolving gas could be observed with the unaided eye after 15 seconds of etching while no gas evolution was seen on the passivated sample. Observations under the microscope revealed attack on the whole

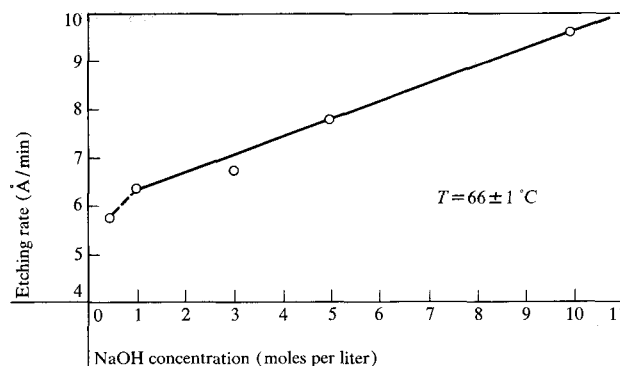


Figure 7 Etching characteristics of thermal SiO₂ deposited on a p-type (111) Si substrate vs NaOH concentration at constant temperature.

surface of the stripped sample, while the passivated sample showed a number of pinholes. This led to the conclusion that a passivation thickness of about 100 Å is sufficient not to be shown as a pinhole by ROH etching. Such a thickness is small in comparison with the average oxide thickness of several thousand angstroms used in bipolar MOS devices, and creates dielectrically weak spots that probably would be shown by the gas evolution technique in the usual voltage range.

Results and discussion

The etching rates of silicon as well as those of SiO₂, vs temperature, follow the known pattern of exponential dependence

$$r = r_0 \exp(-E_a/kT).$$

From the Arrhenius plot in Fig. 6, it is evident that in the temperature range below 90°C, the SiO₂ is etched at a much lower rate than silicon. The p-type silicon doped with boron to about $8.5 \times 10^{19} \text{ cm}^{-3}$ is etched nearly 100 times faster than SiO₂ at 90°C and about 8.5×10^2 times faster at 60°C. The n-type material is etched faster by factors of about 2.3×10^2 and 2.5×10^3 at corresponding temperatures.

The activation energies obtained from the plot are $E_a \approx 0.85 \text{ eV}$ for n-type material ($\approx 4.0 \times 10^{19} \text{ cm}^{-3}$), and $E_a \approx 1.15 \text{ eV}$ for p-type material ($\approx 8.5 \times 10^{19} \text{ cm}^{-3}$). For SiO₂, $E_a \approx 1.23 \text{ eV}$.

The effect of etchant concentration at constant temperature is illustrated in Fig. 7. It shows that to accelerate the etch rate by a factor of 2, the concentration must be increased by an order of magnitude.

• Effect of the size of discontinuity

The etching rate determines the time of etching necessary to obtain characteristic marking pits. For circular discontinuities the size (diameter) can be taken as the parameter. However, since discontinuities may have any

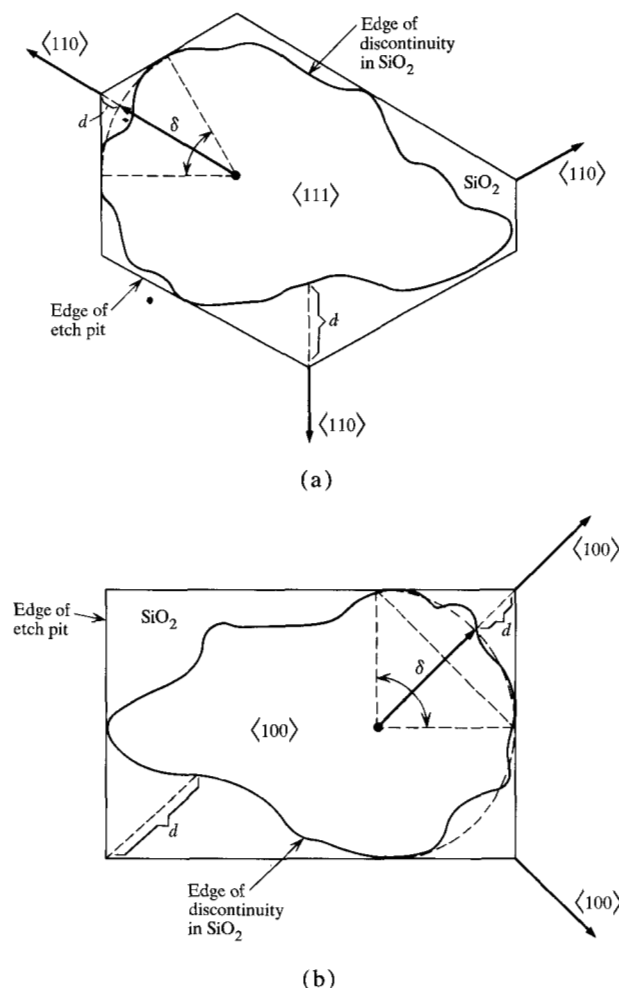
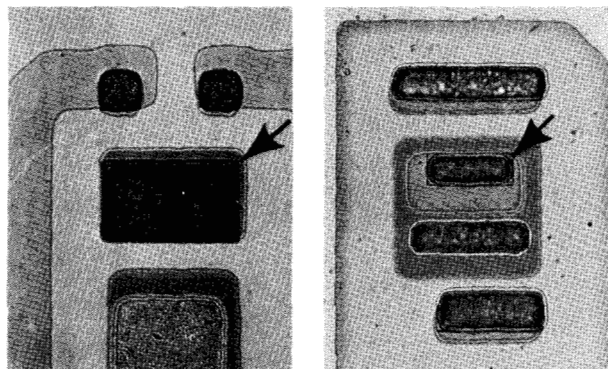


Figure 8 Relation between averaged radius of curvature δ and etching distance d for a random shape of discontinuity in SiO_2 on: (a) $\langle 111 \rangle$ substrate; (b) $\langle 100 \rangle$ substrate.

Figure 9 Openings of different sizes in SiO_2 (contact windows). The arrows indicate points of intersection of two $\{111\}$ planes, which shape the silicon etch pits into rectangles within an etching time of 20 minutes at 75°C in 2.5 molar solution. Underlying material n^+ , $\langle 100 \rangle$ oriented silicon (originally $1000\times$).



shape as well as orientation, the averaged radius of curvature δ is the parameter used here (Fig. 8). This approach is valid for any shape or size of discontinuity, including cracks. For any substrate orientation, the distinctive shape is assured by etching until apexes of the marking pits are revealed. Since the apexes are the most distant points with regard to the edges of an SiO_2 discontinuity, the time necessary to etch the furthest apex is the minimum time to be applied to expose a discontinuity. Figure 9 illustrates this point; two windows in SiO_2 on the same type of substrate material are exposed in the same etching time despite their difference in size.

The radius of curvature is averaged around the direction of an apex within a 90° angle for a $\langle 100 \rangle$ substrate and a 60° angle for $\langle 111 \rangle$ orientation. For these substrates the etching rates in the $\langle 100 \rangle$ and $\langle 110 \rangle$ direction, respectively, determine the shortest time of etching. Therefore, the averaged radii of curvature of the periphery of a discontinuity in those directions determine the distance to which the silicon has to be etched to create the characteristic marking pit.

From Fig. 8 it follows that the etching distance d is related to the average radius of curvature δ in the following ways:

$$d = \delta(\sqrt{2} - 1) \quad \text{for a } \langle 100 \rangle \text{ substrate,}$$

and

$$d = \delta \left(\frac{1 - \sin 60}{\sin 60} \right) \quad \text{for a } \langle 111 \rangle \text{ substrate.}$$

From concurrent etching of silicon of basic low index orientations, the rate has been found to follow the inequality $r_{\langle 111 \rangle} < r_{\langle 100 \rangle} < r_{\langle 110 \rangle}$. Figure 10 represents the relation among time of etching, temperature and averaged radius of curvature δ for $\langle 100 \rangle$ material.

• Effect of lattice imperfections

Figure 1(f) shows the surface of a crystal distorted by mechanical working. The picture represents a $\langle 100 \rangle$ oriented wafer after etching to determine the presence of SiO_2 discontinuities. As can be seen, the etch pits are distorted slightly at the dislocation network lines but without total loss of their distinctive character, so the discontinuities still can be identified. Figure 11 represents a boron diffusion region where the impurity concentration of about $3 \times 10^{20} \text{ cm}^{-3}$ has resulted in lattice distortions that are expressed in the surface roughness (boron pitting). From the symmetry it is evident that the geometry of the etch pits, marking SiO_2 discontinuities, is not distorted by high doping levels.

Summary

Single-component aqueous solutions of NaOH and other hydroxides of alkali metals anisotropically etch intrinsic

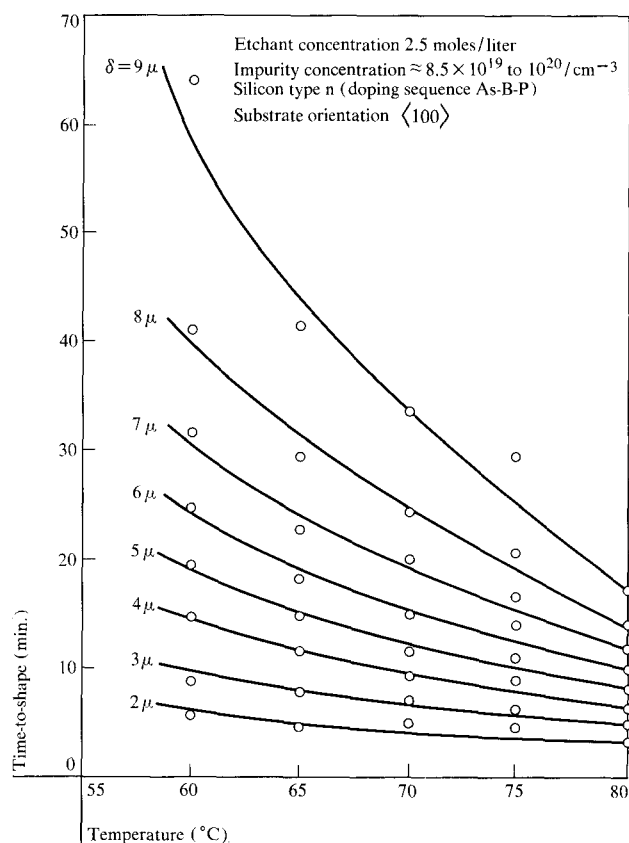


Figure 10 Time to expose a SiO_2 discontinuity vs temperature with averaged radius of curvature δ of an edge of the discontinuity around $\langle 100 \rangle$ as a parameter.

and extrinsic silicon up to a doping level of about 10^{20} cm^{-3} , which corresponds approximately to the solid solubility limit of As, P and B in silicon. The ROH etchants can be applied as a tool for pinhole detection in passivating oxides as well as for determination of the size and shape of a discontinuity. The time required to etch the geometrically characteristic pit for a given substrate orientation at a selected temperature is related to the size of the opening in the oxide, thus allowing its estimation. The possibility of etching in a relatively short time and the simplicity of the method make the etchants a suitable tool for quality control.

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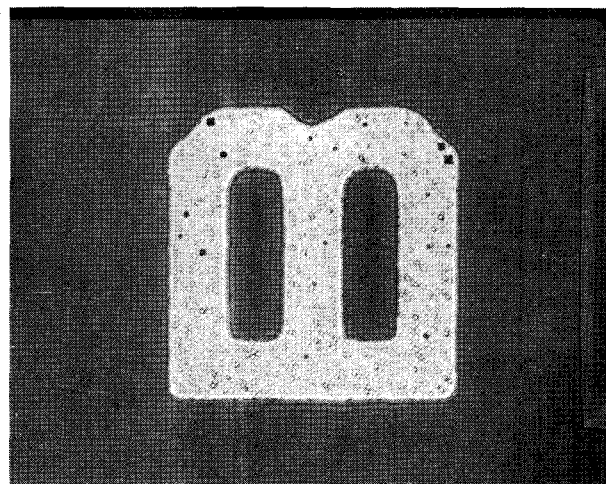


Figure 11 Boron doped region (letter B) with tiny squares marking SiO_2 discontinuities. Surrounding material is epitaxially grown n-type silicon. Boron doping level is $\approx 3 \times 10^{20} \text{ cm}^{-3}$, crystal orientation $\langle 100 \rangle$ (originally 1000X).

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