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Plasma etching as a diagnostic technique in silicon surface studies

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This paper describes a new application of plasma etching, namely as an aid to the characterization of specular semiconductor surfaces. The technique, which is simple and quick to perform, consists of subjecting the semiconductor slice to a brief etching treatment in a fluorocarbon plasma at low pressure, followed by inspection of the surface, using Nomarski microscopy. The whole operation is designated diagnostic plasma etching (DPE). Suitable etching times lie in the range 1 to 6 min and, under the operating conditions described, up to 3 μm silicon is removed, although generally the aim is to remove the minimum amount consistent with good image contrast under the microscope. When examined at high magnification, plasma-etched surfaces display a variety of artefacts, which can be related to features such as contamination and mechanical damage sites. The DPE technique possesses a high level of sensitivity and is capable of providing information on surface condition, not obtainable by existing wet chemical tests or high resolution microscopy, as exemplified by the detection of disturbance of surfaces cleaned by mechanical scrubbing techniques.

1. Introduction

The properties of gaseous plasma have been known for some time but it is only in the last few decades that plasma chemistry has begun to emerge as a technology, finding application in the fields of biology, polymer and analytical chemistry and, more recently, in the semiconductor industry. To meet the growing demand for professionally designed equipment which could be operated by unskilled personnel, several manufacturers have developed plasma processing machines.

Gaseous plasma consists of ions and neutral activated species, which are created by the decomposition and excitation of a gas by a continuously applied r.f. field. In practice, this is carried out in a metal or silica reaction chamber which is maintained at a relatively low pressure by a vacuum pump, while a controlled low flow of gas is admitted. Under these conditions, a constant concentration of active species is maintained.

In this environment of free radicals, many reactions not otherwise achievable, may be performed; other reactions proceed at much lower temperatures than are normally required. Thus silicon can be readily etched in a tetrafluoromethane plasma at temperatures less than 200° C:

$$CF_4 \rightleftharpoons CF_3^* + F^*$$

$$Si + 4F^* \rightarrow SiF_4.$$

Silicon dioxide also reacts with the same plasma but at only one tenth of the rate for silicon [1].

$$SiO_2 + 4F^* \rightarrow SiF_4 + O_2$$

The almost limitless choice of gases which can be used in a plasma system allows a wide range of reactions to be carried out. Many examples of the practical application of plasma reactions may be found in the literature: e.g. plasma cleaning of metal surfaces [2], strong adhesive bonds via plasma treatment [3], photoresist stripping [4], restoration of optical properties of surfaces [5].

Heinecke considers the control of relative etching rates of silicon and silicon dioxide [1]. Devaney and Sheble [6] examine the use of plasma etching in integrated circuit production as an alternative to wet chemical processes but specific applications of plasma reactions to semiconductor technology are not yet extensively documented in the literature. A great deal of expertise and experimental data undoubtedly reside in the laboratories of the companies developing plasma equipment, for instance, L.F.E., I.P.C. and Tegal but little of this is published, for obvious reasons. However, from time to time technical bulletins allied to new or improved processes are issued but normally these are only available to prospective customers. However, the present paper is concerned with an entirely new application of plasma etching, i.e. as a diagnostic tool.

A study of the kinetics of fluorocarbon plasma reactions with polished silicon surfaces had shown that material removal versus etching time characteristics were linear. This held true even for etching times of only a few minutes but, on some occasions, there was evidence of an initiation effect. In the course of a closer investigation of this phenomenon, it was observed that features were revealed on the slice surface which, in some cases, were directly traceable to preceding processes or mishandling. Further experimental work revealed that brief plasma etching, followed by high resolution microscopy was an extremely sensitive technique for characterizing polished semiconductor surfaces, or processes which had been carried out on them.

In the following, the technique is described in detail and three examples of its application are presented. A discussion of the results follows in which explanations of the observed phenomena are proposed.

2. Experimental

2.1. Details of the technique

The technique essentially consists of subjecting the slice to a brief etch in fluorocarbon plasma and examining the etched surface by interference contrast microscopy. The complete operation will subsequently be referred to as diagnostic plasma etching (DPE).

The plasma-etching equipment used in the work described below was a standard commercially available apparatus, the PDE/PDS Type 1002, supplied by the L.F.E. Corporation. It has twin 8 in. diameter silica reaction chambers and the r.f. field is applied inductively by means of coils wound around the outside of the chamber. Plasma source gas is fed into the chamber via four manifolds located immediately adjacent to the inner wall. A vacuum pump evacuates the chamber through an orifice in the end of the chamber.

Slices to be processed are held vertically in a silica jig within a perforated metal tunnel inside the chamber. The tunnel screens the work piece from unwanted electrically charged species and damaging ultra-violet radiation but allows passage of the uncharged activated species necessary for the reaction.

For much of the work, DE100, a proprietary etching gas mixture of tetrafluoromethane (major constituent) and oxygen, supplied by the L.F.E. Corporation, was used but successful results have also been obtained with pure CF_4 and other CF_4-based gases.

Typical operating conditions were as follows: slices were etched singly in the centre of the chamber whose pressure was maintained at 2 Torr against an etching gas flow of $40\,\mathrm{ml\,min^{-1}}$. R.f. power applied was 200 W at 13.5 MHz and the etching time was 5 min. The amount of material removed under these particular conditions was up to $2\,\mu\mathrm{m}$ per side. How well specific surface features are delineated will, of course, be related to the etching conditions but, broadly speaking, the material removal will be in the range of a fraction of a micrometer to about $3\,\mu\mathrm{m}$.

The microscope used for inspection of the plasma-etched surfaces was a Reichert Zetopan, fitted with a Nomarski illumination system. Overall magnifications of $\times 70$ to $\times 130$ were used for most of the work. Photomicrographs were produced on the same microscope, while macrophotographs of whole slices were taken with a Polaroid MP4 camera system.

2.2. Details of specimens

The specimens which were used as vehicles for the DPE work derived from in-house manufacture and external sources. The in-house polished slices were produced by conventional methods from 50 and 75 mm diameter zero dislocation density {1 1 1} Czochralski silicon crystals of resistivities ranging from $10\,\mathrm{m}\Omega\mathrm{cm}$ to $10\,\Omega\mathrm{cm}$ (n- and p-type). Wafers cut from the crystals were chemically etched, then single-side polished with an alkaline silica colloid or a zirconia suspension, on a synthetic suede pad. The polished slices were subjected to a rigorous series of wet chemical cleaning operations, followed by washing in high purity water and finally spin drying.

The polished slices from external commercial sources had been supplied to the semiconductor industry's highest standard of cleanliness (see Section 3.1). Accordingly, these were examined immediately after unpacking, without further cleaning.

3. Applications of diagnostic plasma etching

3.1. Assessment of surface quality of as-received polished slices

The increasing mass of evidence which has appeared during the last few years, linking the properties of silicon surfaces with the performance and yield of devices fabricated thereon, underlines the important role of surface quality of the input slice in silicon device technology.

The evaluation of surface quality of polished silicon surfaces involves making an assessment of two categories of defect:

(1) contamination, in the form of isolated particles, or a continuous film of foreign substance on the surface of the slice;

(2) visible blemishes, such as scratches and haze. The latter is apparent as a mistiness of the surface under certain lighting conditions and arises from the presence of microscopic surface irregularities such as pits, mounds or particles, which scatter the light.

Today it is standard practice to inspect slice surfaces with the naked eye, by spotlight illumination in a darkened, dust-controlled enclosure. Ambient air cleanliness is to Class 100 standard [7] which specifies no more than 100 airborne particles of 0.5 μm diameter or greater, per ft^3. The highest quality slices used in the semiconductor industry are typically required to have no more than 10 mm total length of scratches, less than 5 contaminant particles and be entirely free of haze.

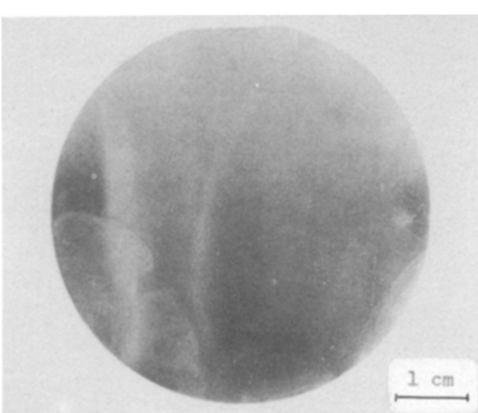


Figure 1 An example of hazy patches generated on a polished slice by DPE.

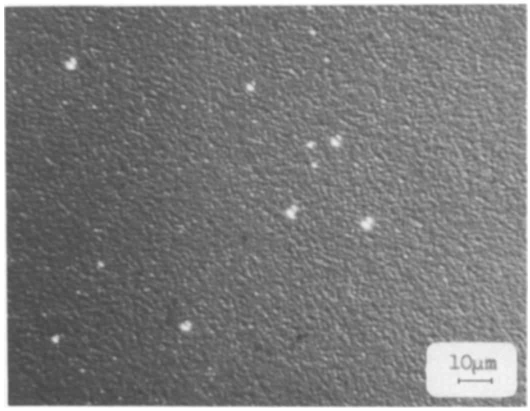


Figure 2 Typical fine structure of haze developed by DPE.

Most of the input slices to DPE were to the above specification, but a few reject slices were also included, with known blemishes, to correlate and record the effect of the DPE on these features.

After DPE, the surfaces typically had the appearance to the naked eye of a faintly hazy mirror. It was rare for the density of haze to be uniform over the whole slice surface and the non-uniformities usually took the form of irregularly shaped patches or streaks (Fig. 1), but the subtle changes in reflectivity perceived with the unaided eye could not always be related to textural variations under the microscope. At magnifications of the order of × 100, the etched surface presented a uniform, granularly textured background, superimposed upon which were discrete microscopic spots (probably pits) of regular shape (Fig. 2), the numbers varying considerably from slice to slice.

Contamination sites and identifiable damage features such as tweezer handling marks which, before DPE had been barely detectable by microscopic examination, were rendered with greatly enhanced clarity by the plasma-etch technique allowing them now to be visible to the naked eye. Many features, totally undetected on the input slices by the usual inspection method, were found to be delineated by DPE. In this category are ultra-fine scratches (Fig. 3) and features associated with the finishing or final cleaning process which the

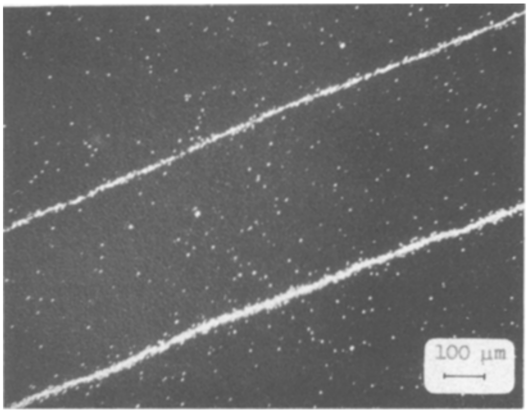


Figure 3 Fine scratches, previously undetectable by standard inspection methods, made visible by DPE.

slice had been subjected to, prior to delivery. The latter are dealt with in greater detail in the following section.

In certain circumstances, DPE was found to generate patterns (Fig. 4) identical to those obtained with specific wet chemical methods for delineating crystal-doping striations [8, 9].

In addition to the features described above, the technique revealed a mass of fine detail, much of which is as yet uninterpreted.

3.2. Study of the effects of particle removal methods

Mechanical scrubbing is widely used for the removal of particulate contamination from planar surfaces and several commercially produced machines are available for carrying out this operation automatically. All incorporate rollers or flat pads of soft material, which are drawn over the surface to be cleaned. A wide variety of pad materials are in use, ranging from synthetic mohair to fine nylon bristle. Chosen liquids may be delivered to the surface and the cleaning process is normally terminated with high speed spin drying. Other process variables are pad loading, speeds of rotation of pad and work surface, frequency of application of the pad and washing times. The more sophisticated machines, particularly those designed specifically for wafer cleaning, incorporate cassette-to-cassette transfer, so that a batch of wafers passes through a programmed cycle of operations without handling.

Two forms of scrubbing machine, illustrated schematically in Fig. 5, were examined by subjecting slices which had been cleaned on them to DPE.

In system A, the slice is held on a vacuum chuck and spun about a vertical axis at 5000 rpm. The scrubbing pad, about 1 cm diameter, is drawn radially across the slice three times, while deionized water is sprayed on the surface. Finally, with the liquid feed turned off, the speed of rotation is increased to 8000 rpm to dry the slice.

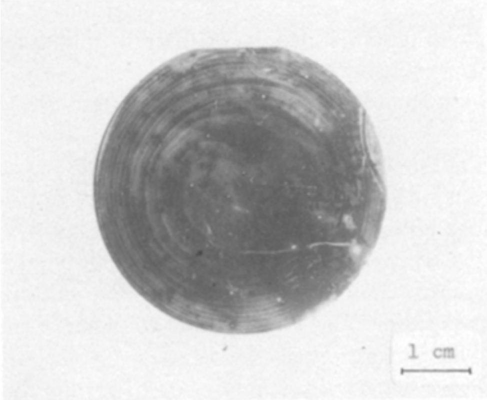


Figure 4 Photograph of a whole slice, after DPE, showing a striated pattern, which is almost certainly related to crystal-doping variations.

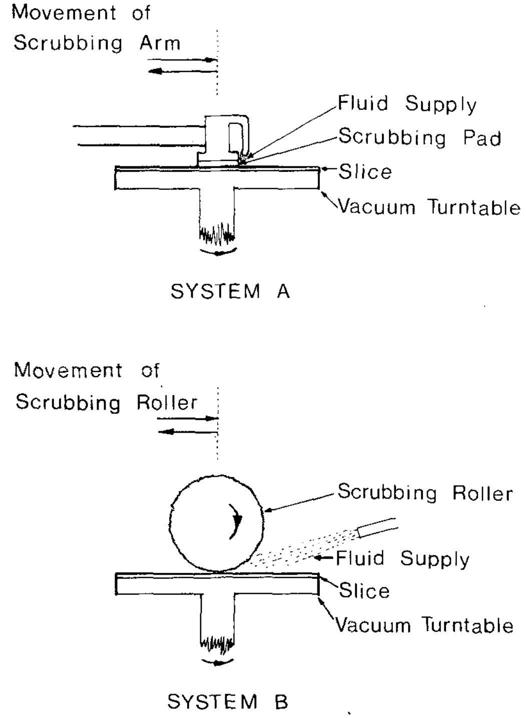


Figure 5 Schematic diagrams of slice scrubbing systems A and B.

In system B, the slice is again held on a spinning chuck but the scrubbing "tool" in this case is a solid roller with the chosen scrubbing material affixed to its curved surface. The roller rotates about a horizontal axis at a speed of 90 rpm and, in the scrubbing cycle, it is drawn diametrically across the slice (the roller is long enough to cover the entire upper surface on a single traverse) whilst a jet of cleaning fluid is directed onto the slice. On the completion of each pass, the roller is automatically cleaned with a scraper blade and a water spray. A wide variety of timing and sequencing of operations is possible on this system but a typical cycle used was:

10 sec scrub with deionized water carrying a trace of detergent

10 sec rinse with ammonium hydroxide solution

10 sec rinse with deionized water

10 sec spin dry.

Diagnostic plasma-etched slices from both cleaning systems manifested the faintly hazy appearance and microscopic spots of the type already described in the preceding section, but in respect to other features the two processes differed markedly.

The general appearance of slices cleaned on system A was of a criss-crossing pattern of spiral lines concentric with the centre of the slice (Fig. 9c) and extending to the edge of the slice. This effect was obtained regardless of the source or resistivity of the silicon slice used and, in all cases, interference contrast microscopy had failed to reveal any trace of the pattern before DPE. There was no observable difference in results when different types of synthetic suede were used for the scrubbing pad but reduced loading on the scrubbing arm was found to give less intense marks. Replacement of the automatic scrubbing arm with a simulated manual scrubbing, using a cotton wool pad, gave rise to the usual spiral pattern after DPE but superimposed upon this were radially directed streaks (Fig. 6). When all scrubbing was omitted and water alone was applied to a rotating slice, no lines radial or spiral, were generated, thus eliminating the possibility that these etching artefacts were associated with residues from the spin-off of water. The possible contribution of impurity transfer from the pad material to the slice during scrubbing was investigated. Before fitting on the machine, the synthetic suede pads were cleaned successively with acetone, isopropyl alcohol and trichloroethane to remove residues of chemicals used in the manufacture of these fabrics. Scrubbing was carried out in the usual way but the same solvents were sprayed on to the slice instead of water. In all cases, after DPE, the same spiral pattern was obtained as with uncleaned pads and water as the irrigating fluid, suggesting that in this instance DPE delineated scrubbing marks were not the result of smeared contamination.

Slices cleaned on system B tended to have higher densities of microscopic spots than those cleaned on system A but were found to be virtually devoid of scrubbing marks of the type developed on system A cleaned slices. When mohair or nylon bristle rollers were used, very few faintly engraved lines were found, with no recognizable pattern. An entirely different effect was observed when a synthetic suede roller was used under otherwise identical conditions. Over-

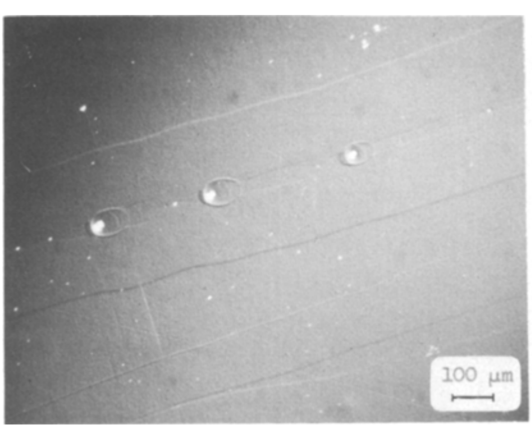


Figure 6 Typical scrubbing marks produced by a manually held cotton wool pad and developed by DPE.

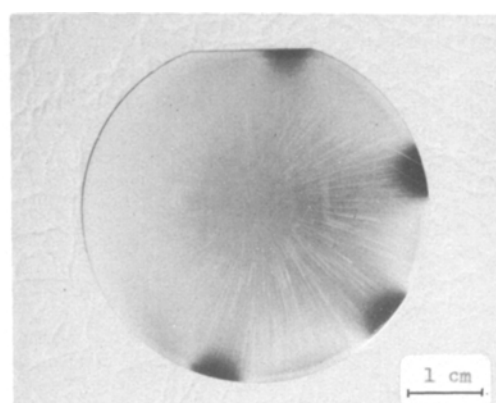


Figure 7 Typical scrubbing marks produced by a synthetic suede roller in system B and developed by DPE.

laying the occasional fine curved line was a regular pattern of shadowy radiating streaks (Fig. 7).

The remarkable difference in surface condition between slices cleaned by the two systems prompted an experiment to examine how the two systems interacted. Slices first cleaned on system A were immediately cleaned on system B, then subjected to DPE. The slices still bore the characteristic spiral pattern and it was clear that system B was incapable of significantly altering the surface condition generated by system A.

3.3. The detection of photoresist residues

This diagnostic application derived from a study which was being made of the plasma etching of silicon and vapour-deposited silicon nitride, using a patterned photoresist layer as a mask. "Windows" in the resist layer were opened by standard wet chemical processing and the exposed substrate surface was critically examined for residues. Even interference contrast microscopy failed to reveal any evidence of contamination in the "windows" but, as a double assurance, the whole "window" cleaning operation, including final inspection, was repeated, with the same result.

However, after DPE, artefacts were apparent on the substrate surface within the "windows" and it was concluded that the history of the photomechanical window-forming process was being retained and revealed in an informative manner by DPE. At the centre of the slice the artefacts were circular in shape (Fig. 8a). With increasing radial distance from the centre they assumed progressively more elongated shapes (Fig. 8b), the long axis of the feature always being parallel to the direction of the slice radius at that point. This phenomenon occurred when silicon or silicon nitride substrates were used and the morphology and distribution of the artefacts suggested that they were related to the spray and spin development process for the photoresist.

4. Discussion

Some impression of the sensitivity of DPE relative to established wet chemical diagnostic methods is useful when considering the above results. This is demonstrated in Fig. 9. depicting areas of three cleaned slices which had been subjected to three different types of preferential etch, respectively 1 min standard Sirtl etch (equal volumes of 50% aqueous chromium trioxide and 48% hydrofluoric acid), 1 min Grieco copper displacement etch [10] and DPE. Sirtl etch revealed only the crystal growth striae and no surface features. The Grieco-etched slice had a more textured surface, together with some scrubbing marks. These were mainly near the centre and it is probable that only the more severely affected areas were delineated. However, on the DPE slice, scrubbing marks were revealed at a considerably higher density and with greater detail in all parts of the slice.

No single mechanism is adequate to account for the generation of the various plasma-etching artefacts which have been encountered. Plasma etching would be expected to respond to discontinuities in the silicon crystal lattice in the same way as wet chemical reagents, namely with localized accelerated action resulting in "negative relief" etch features such as pits, hollows and V-trenches. Crystal growth defects, work damage

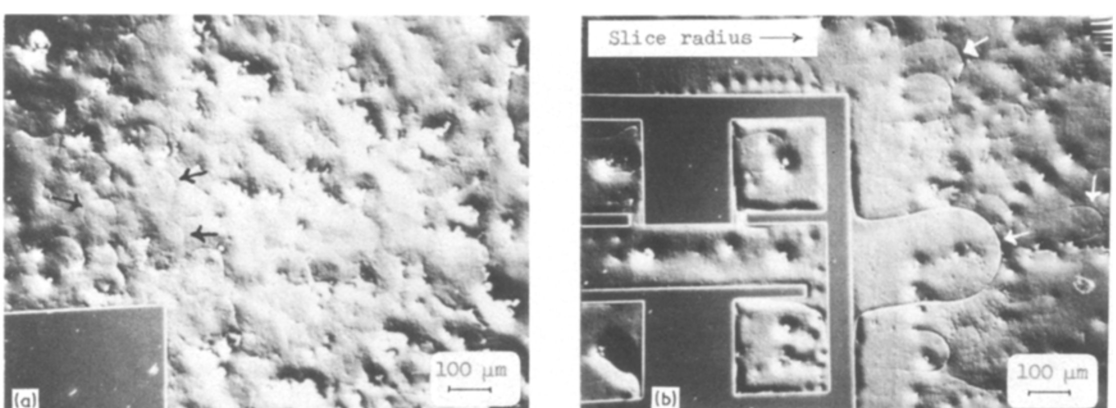
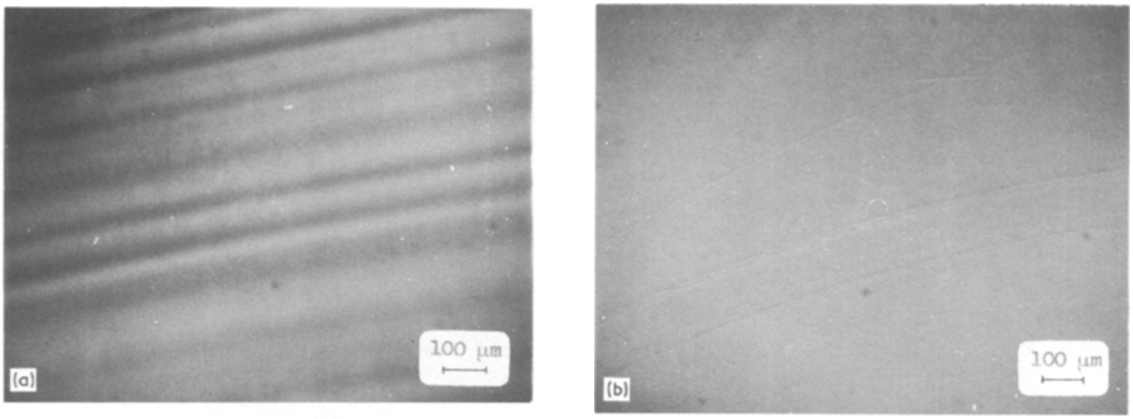


Figure 8 Artefacts revealed in photomechanically fabricated windows by DPE (a) near the centre of the slice and (b) at about 5 mm from the edge of the slice. Examples of the features discussed in the text are arrowed.



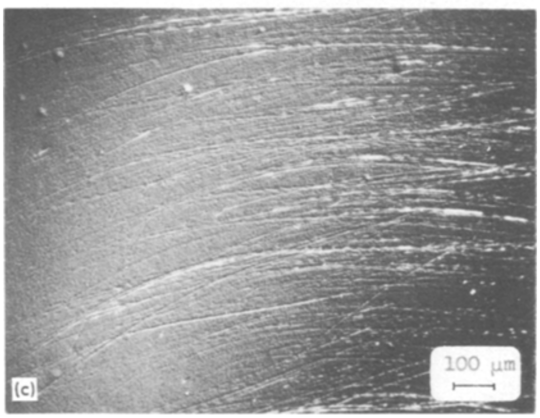


Figure 9 Comparison of the surfaces of three identically prepared slices (system A scrubbed) which were then respectively subjected to (a) Sirtl etching, (b) Grieco etching and (c) DPE. The area depicted in (a) is located a few mm from the edge of the slice, where the doping striation pattern was most strongly developed. The fine texture of the surface portrayed here is, however, typical of the whole slice. The areas in (b) and (c) were both situated about 10 mm from the centre of the slices. Slice orientation is comparable in all three cases.

and non-uniformities in dopant distribution would give rise to such artefacts and some of these have been observed. It is also conceivable that certain materials present as contaminant particles on or embedded in the silicon surface could affect the silicon–fluorocarbon plasma reaction, again resulting in selective etching.

The presence on the silicon surface of material which is more slowly attacked by the plasma than silicon, or is completely inert, will exercise a masking effect and "positive relief" artefacts such as mounds, mesas and ridges result. Process residues and extraneous contaminants would give rise to such features. The foreign body may be removed during the plasma etch but, if inert, could persist. On one occasion it was observed that a microscopic fibrous particle of unknown composition, accidently deposited on a silicon surface,

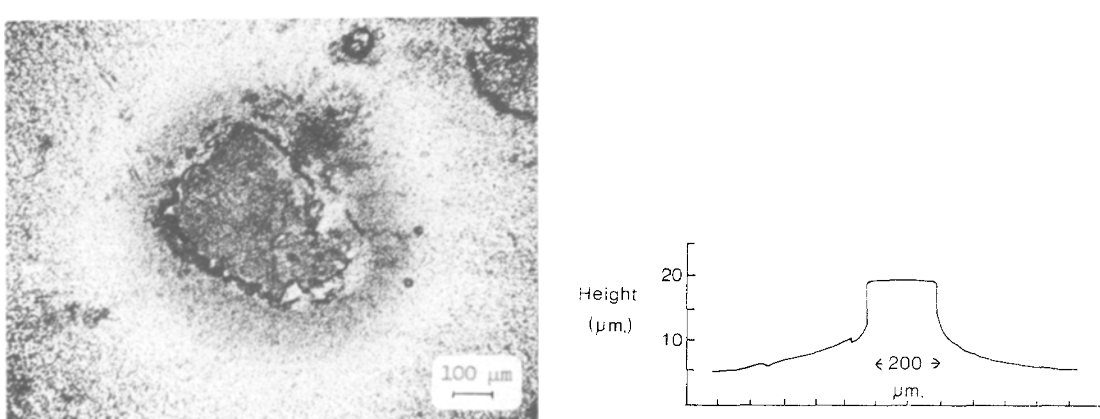


Figure 10 Photograph and Talysurf profile of a mesa resulting from masking of the surface by an inert fibrous particle during a long plasma etching treatment.

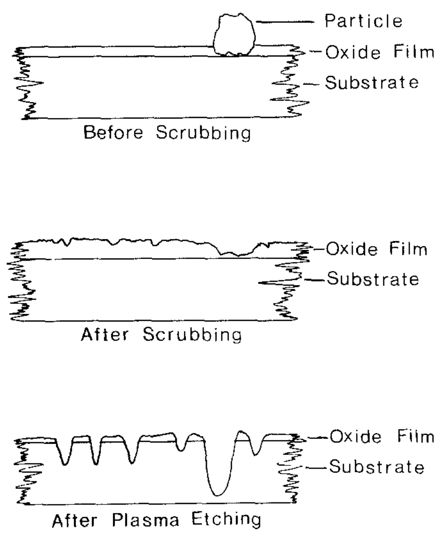


Figure 11 Schematic diagram of the proposed model for oxide disturbance by mechanical scrubbing, followed by DPE (no vertical scale implied).

survived several etching cycles totalling more than 1 h exposure. The particle, which was obviously resistant to the attack of both fluorine and oxygen plasmas, was eventually removed by hand, leaving a mesa 15 μm high (Fig. 10).

The scrubbing artefacts are not thought to be related to direct damage of the silicon surface which, at first sight, appears to be the case. Here we believe that the scrubbing operation abrades the natural oxide on the silicon surface. Perturbations in the oxide thickness thus produced lead to it being etched through more rapidly in some regions than in others during DPE. The pattern of the original abrasion marks in the oxide is thus carried through into the silicon but the more rapid etching of silicon, which was commented upon in Section 1, brings about a ten-fold magnification of relative depths (Fig. 11), thus effectively extending the height resolving power of the interference contrast microscope from 30 Å to 3 Å. Strong evidence in support of this hypothesis was provided by an experiment in which system A scrubbed slices were boiled in concentrated nitric acid then plasma etched. No spiral scrubbing marks were found on any of the etched slices. It is inferred that scrubbing abrasions in the natural oxide were "healed" by this oxidation treatment; therefore no artefacts were developed.

As already stated, DPE reveals a wealth of detail not seen by other surface evaluation methods and many of the artefacts observed are not yet explained. For instance, the radial streaks on slices cleaned on system B using an artificial suede roller (Fig. 7) but absent when a mohair roller was used. Another example is the origin of the microscopic pits, which might be from vacancy clusters or fine residual work damage sites.

5. Conclusions

Diagnostic plasma etching is a powerful technique for the assessment of surface quality of specular silicon, silicon oxide and silicon nitride surfaces. It is particularly applicable to studies of residual contamination and the interaction of mechanical processes and slice surfaces. In a quality assurance function on the input slice to device production, it is capable of providing valuable information about surfaces, which cannot be obtained by existing inspection methods.

The technique possesses a high order of sensitivity compared with existing wet chemical methods of evaluating surfaces and has the advantages of being quick and easy to perform and involves no hazardous materials. The mode of formation of many of the observed plasma etch features can be explained but some artefacts are still to be interpreted.

The present study is by no means complete; subsequent experimental work in this laboratory indicates that DPE can also be applied to germanium. With variations of plasma-etching gas and operating conditions, the scope of the technique could probably be extended to other materials, particularly the compound semiconductors and metals.

6. Acknowledgements

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