

Use of silane-based primer on silicon wafers to enhance adhesion of edge-protective coatings during wet etching: Application of the TALON Wrap™ process

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ABSTRACT

Hydrolyzed silane primer solutions were made of an organosilane in glycolether diluted with a large amount of water with or without an acid as a catalyst. The newly developed primer compositions exhibited an extended shelf life of 3 months or more. The compositions were specially designed to accommodate ProTEK™ layer adhesion in the TALON Wrap™ process. In this application, a spin-coatable polymeric material, ProTEK™, is applied as the protective coating to coat the top, edge, and underside rim of the wafer in preparation for backside etching. By applying an underlayer of primer and an overlayer of ProTEK™ coating to the top, edge and the bottom side rim of the wafer, an effective encapsulation of the wafer was achieved by using a custom-designed baffle. Each layer was applied by spin coating followed by baking at a wide temperature range. Thermal processing was followed by wet etching in KOH at an elevated temperature for ≥ 10 hr. Post-etched wafers were rinsed with deionized (DI) water. Excellent edge profiles without “knife-edges” were obtained after etching the unprotected areas of the wafer. The process is fully automated because it is carried out in the TALON™ automated wafer-processing tool. Intact films with no lifting or peeling were obtained during or after the KOH etch process/DI rinse for silicon substrates.

Keywords: Organosilane, primer, adhesion promoter, KOH wet-etch, etch protective coatings, ProTEK™ coating, TALON Wrap™ process

1. INTRODUCTION

Temporary etch protective coatings are used to protect CMOS-MEMS circuitry during deep silicon etches that use hot concentrated potassium hydroxide (KOH) or other alkaline solutions. The primer solutions described here were specifically designed and developed to enhance adhesion of temporary etch protective coatings to rough silicon substrates during harsh wet-etching processes. In addition, the silane-based primer solutions performed successfully in the TALON Wrap™ process (developed by Brewer Science), which is a method for protecting the edge of the semiconductor wafer by applying a layer of etch protective material simultaneously to the top, edge, and bottom side-rim of the wafer. Single-side polished wafers are commonly used for these applications, wherein the average back-side roughness of a 100-mm wafer is $3.59 \mu\text{m}$; and for a 150-mm wafer, $2.22 \mu\text{m}$. The silane-based primer solution must promote good adhesion for the ProTEK™ coating topcoat on both smooth and rough silicon surfaces (wafer front-side and wafer back-side). Once the protective coating is applied with good adhesion, it effectively protects the coated areas of the wafer, including the wafer’s edge, during wet etching processes. The protective layer wraps the wafer from the top side and prevents the material on the edge of the wafer from lifting during etching, thus preventing formation of a “knife-edge” on the wafer.

1.1 Hydrolyzed silane primer solutions: Adhesion promoter

Organosilanes are hybrid organic-inorganic compounds. They are used as coupling agents across the organic-inorganic interface to enhance the interfacial adhesion.¹ In general, each primer composition was made up of 1-3% organosilane, such as phenylsilanes in 50-80% glycol ether and 20-40% water, and 0.1-2% acid catalyst. Whenever needed, freshly distilled organosilane was employed. The main reaction (hydrolysis) is transformation of Si-OCH_3 to Si-OH (silanol) as indicated in Figure 1. Condensation reactions of the silanol may occur after hydrolysis to form dimers, oligomers, and polymers. Our goal was to devise a system in which the rate of hydrolysis is substantially greater than the rate of condensation. Acetic acid was added as a catalyst to accelerate hydrolysis and to stabilize the primer solution. It was found that using an acid catalyst accelerated the rate of hydrolysis considerably. The degree of hydrolysis of primer

solutions was monitored through gas chromatography (Figures 2, 3).

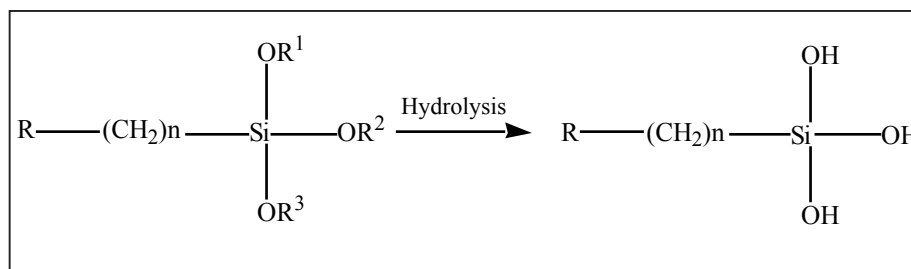


Fig. 1. Primer chemistry: R = aromatic group; R¹, R², R³ = alkyl group.

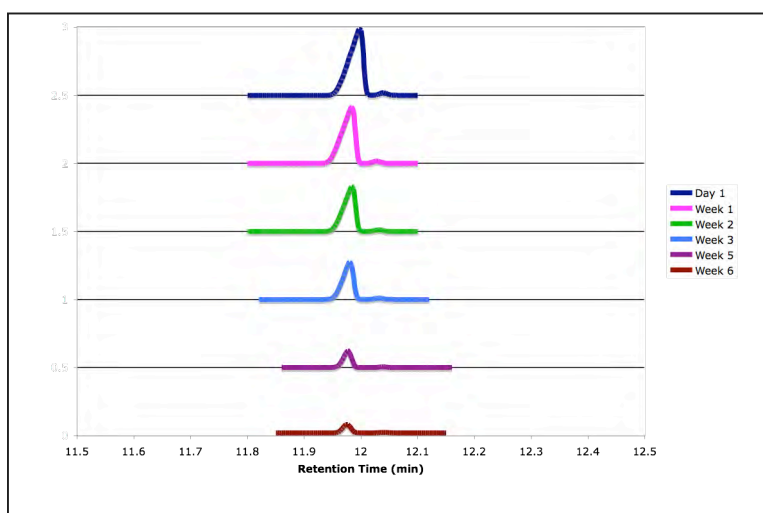


Fig. 2. Hydrolysis of primer without acid (JM0908-1) at room temperature.

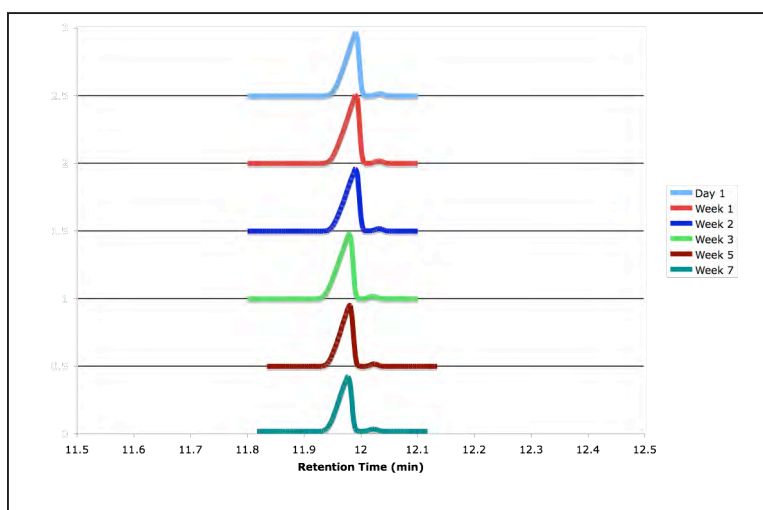


Fig. 3. Hydrolysis of primer without acid (JM0908-1) at 0°C.

A gas chromatography method was developed to analyze primer solutions on a weekly basis until complete hydrolysis (100%) was achieved. The primer solutions were injected at 160°C by using a flame ionization detector (FID). The main

component arising from unhydrolyzed silane was eluted at 12 minutes, whereas the Si-OH group was undetectable by GC. As the hydrolysis proceeded, the peak of interest (at 12 minutes) diminished (Figure 2). The degree of hydrolysis was calculated by taking the ratio of the peak area (at 12 minutes) of aged primer solution to that of fresh primer solution.

It was found that using an acid catalyst accelerated the rate of hydrolysis considerably. For example, by adding 0.5% by weight acetic acid to the primer formulation, the silane in the primer solution was completely hydrolyzed within 1 day of making the formulation. Although the silane in the primer solutions made without an acid catalyst (e.g. JM0824-1, JM0908-1) was hydrolyzed slowly and took several weeks (Figure 2) to achieve complete hydrolysis, this primer solution performed successfully from within 1 day of making it. Once made, no standing time was required for the primer solutions. The slowest rate of hydrolysis was observed for the primer formulations stored at 0°C-1°C (Figure 3). It was noted that primer solutions that contained an acid catalyst always remained clear with no haze or cloudiness, whereas the primer solutions made without an acid catalyst became cloudy at one stage during storage. A design of experiment was conducted to optimize the primer formulations with or without acid.

1.2 ProTEK™: Etch-protective polymeric material

Commercially available ProTEK™ temporary etch-protective coating² (Brewer Science) was used. At room temperature (RT) this material is highly soluble in an environmentally friendly solvent and was conveniently applied as thin films by the spin-on method. It has excellent chemical resistance to KOH and can provide etch protection in hot KOH solution for more than 8 hours. Typical applications are front-side substrate protection during back-side V-groove etch processing, and front-side substrate protection for wafer thinning processes. Discussion of the mechanism for the primer-ProTEK™ coating interaction is beyond the scope of this paper.

1.3 Preparation of etch-protective coating

The primer solution in section 1.1 was spin coated onto a silicon wafer. For front-side wafer coating, the solution was applied at 1500 rpm for 60 seconds; for back-side coating, the solution was applied at 2000 rpm for 60 seconds. The wafer was baked at 130°C for 60 seconds. Then the ProTEK™ B1-25 etch protective coating solution was spin coated on top of the primer layer at 1500 rpm for 90 seconds for front-side coating, and at 2000 rpm for 30 seconds for back-side coating. The protective coating was baked at 100°C for 2 minutes, followed by baking at 130°C for 2 minutes and then at 205°C for 60 seconds for front-side coating. If the back-side of the wafer was being coated, then a single bake at 205°C for 2 minutes was sufficient. The protective coating thickness is very much dependent on the standing height of each sensitive device structure that requires protection during etch. Typical protective coating thicknesses of from 3 to 12 micron will accommodate most applications.

1.4 Wet etching of silicon wafer prepared with protective coating

The wafer prepared in section 1.3 was etched in 30% aqueous KOH solution at 85°C for 2 to 3 hours. After the wafers were etched and allowed to cool for 15 minutes, the wafers were rinsed two to three times in deionized (DI) water. The protective coating remained intact. No lifting or peeling was observed during or after etching or rinsing. After etching was completed, it was necessary to remove the ProTEK™ protective coating. It was removed by submerging the wafer into a bath containing ProTEK™ remover for 20 minutes at 23°C. A second bath consisting of the same formula and process was repeated, which was followed by soaking the wafer in IPA for 5 minutes and then air-drying it.

1.5 Shelf-life test of a primer without acid catalyst

The primer solutions (e.g. JM0908-1 and JM0824-1) were stored at room temperature and tested on a weekly basis by following the procedures described in sections 1.3 and 1.4. For up to 3 months, the primer solution performed well (0 mm lifting during/after KOH or DI water rinse). It was noted that during this storage period, this primer solution became cloudy temporarily at one stage, which indicated incomplete hydrolysis.

1.6 Shelf-life test of a primer with acid catalyst

The primer solution with acid (JM1003-5) was stored at room temperature and tested on a weekly basis. It was found that this primer solution performed well (0 mm lifting during/after KOH or DI water rinse) for more than 3 months. In contrast to the primer solution described in section 1.5, the primer containing an acid always remained clear with no haze or cloudiness, which confirmed the dual role of the acid as a catalyst and a stabilizer.

2. TALON Wrap™ PROCESS

Earlier report² on the protective coating materials describes how ProTEK™ protective coating materials were successfully used to coat smooth front-sides of silicon wafers for wet-etch processes. However, in the Talon Wrap™ process, four coats of ProTEK™ Primer (Brewer Science) had to be applied to provide sufficient adhesion of the ProTEK™ protective coating material onto the highly rough wafer backside. To overcome this issue, the ProTEK™ primer structure was tailored to meet the specific requirements of the TALON Wrap™ process. It was found that only one coat of the newly developed primer and of the protective layer was sufficient to promote adhesion during extended hours (≥ 10 hr) of wet-etching processes.

2.1 The Process

The TALON Wrap™ process is a method to protect the edge of the semiconductor wafer by applying a layer of etch-protective material simultaneously to the top, edge, and the bottom side-rim of the wafer. It provides an effective edge protection of the wafer during etching processes. As indicated in Figure 4, the protective layer wraps the wafer from the top side and prevents lifting of the material at the edge of the wafer during etching, which in turn prevents the formation of a “knife-edge.” The back-side dispense is a fixed position nozzle, therefore wafers with a flat will have an offset between the innermost point of the flat and the remaining portion of the wafer. As indicated in inset A of figure 4, 5 mm of protective material were applied to the innermost point of the wafer flat, leaving the remaining part of the wafer with 8 mm of protective coating. If notched wafers are used, this offset no longer applies.

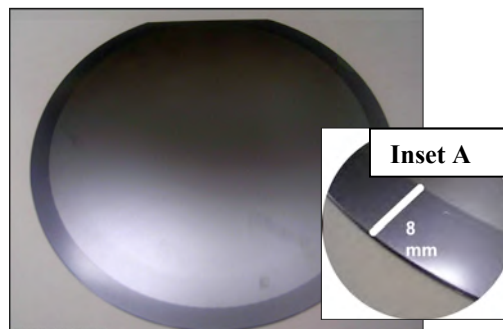


Fig. 4. The bottom-view of a 150-mm wafer edge-wrapped with primer JM0824-1 and ProTEK™ B1 coating. Inset A showing the edge view of the wrapped wafer

A baffle³ was designed to successfully wrap the edge of a wafer. The coating material accumulates in the baffle, and the baffle helps to coat the edge of the wafer. Figure 5 demonstrates the spin-coating process using a baffle to achieve edge protection. ProTEK™ coating was spin-applied by using dynamic dispense (Figure 5a and 5b); at the same time ProTEK™ coating material was dispensed through backside dispense arm to coat the underside of the wafer (Figure 5c). The wafer was placed on pins on the hot plate for proximity bake (Figure 5d). The final spin-coated wafer was ready with its edge and underside rim protected (Figure 5e).

The purpose of this baffle is to collect the excess material during spin coating, and to coat the material along the edge of the wafer, to obtain a seamless, continuous coating at the edge of the wafer.

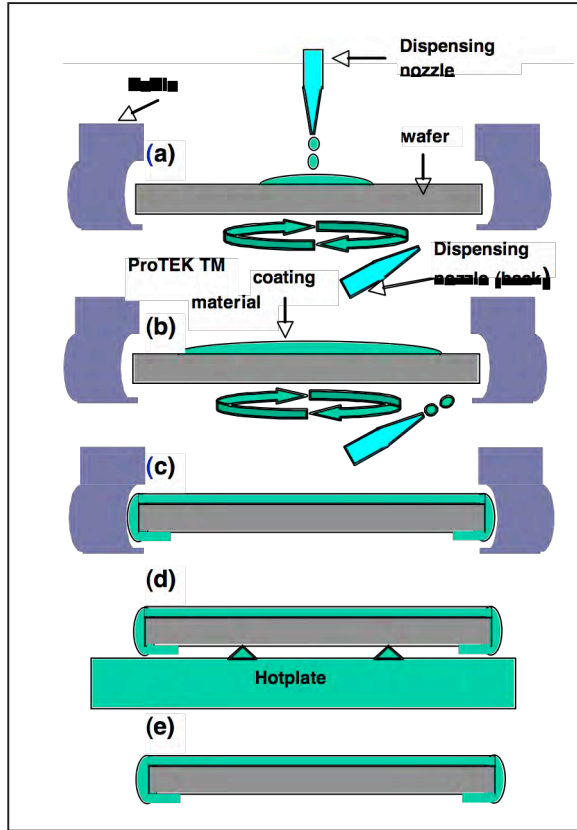


Fig. 5. Edge protection using a baffle.

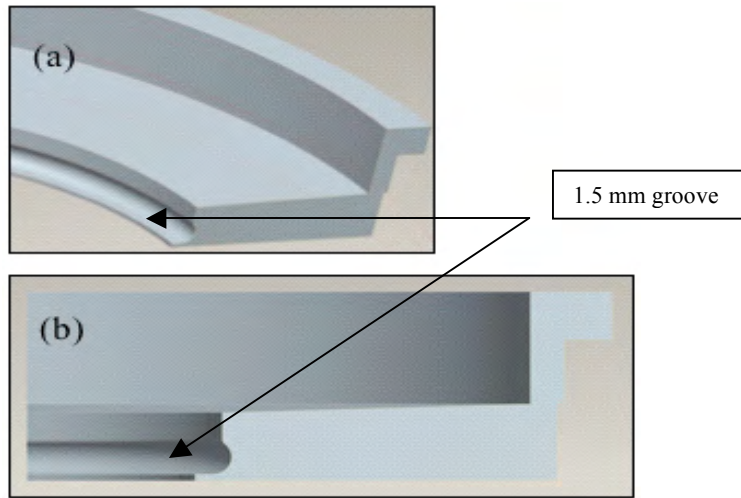


Fig. 6a and b. 3-D CAD views of baffle.

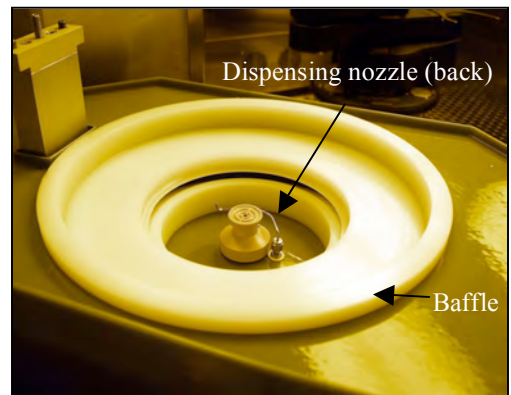


Fig. 7. Photograph showing the baffle and back-side dispensing nozzle on the spin coater.

Figure 6a and b shows a three-dimensional CAD view of the baffle. A back-side dispenser simultaneously coats material on the back-side rim of the wafer. After the spin-coating process, the wafer is baked on a hot plate using a proximity bake method. After the bake, a seamless coating of the front side, edge, and back-side rim of the wafer can be observed.

The spin-coating module is configured with the wrapping baffle and backside dispense nozzle as shown in Figure 7. The innermost point in the baffle groove sits 1.5 mm from the wafer edge. When a spin speed of 2000 rpm is reached, the expelled material flowing off of the wafer surface accumulates in the baffle groove, providing material contact to the wafer edge. After several seconds at the nominal rotational speed, the material flows out of the bottom edge of the baffle groove and into the spin module waste drain.

Fully automatic TALON™ 200 wafer processing tool (Brewer Science) was used with the special wrap baffle to conclude our studies. In this study, we configured the thermal modules with a 0.005" gap between the thermal module surface and the wafer. This configuration prevents contact from occurring between the coated under-side rim of the wafer and the thermal module surface.

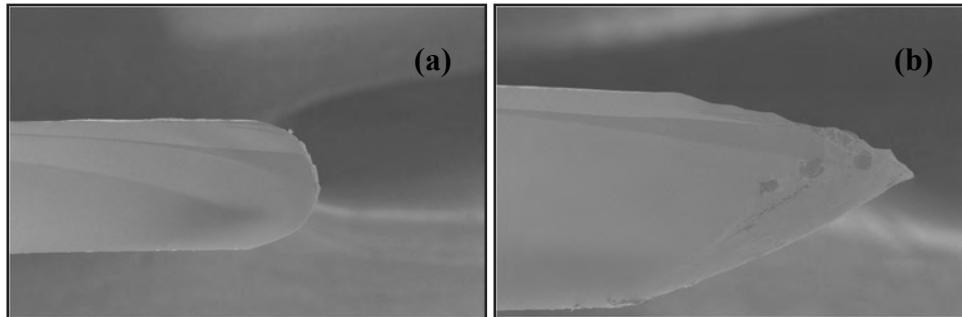


Fig. 8. Without edge wrap, top surface only is coated (edge view of a silicon wafer). a. Wafer coated with primer and ProTEK™ coating before KOH etch. b. Wafer from 8a after KOH etch and removal of ProTEK™ coating.

Failure to adequately protect the wafer's edge during the wet-etch processing steps will cause a knife edge phenomenon to occur, as shown in Figure 8a and b. This knife edge phenomenon can cause a multitude of problems, which vary from 1) wafer instability, which increases substrate breakage during normal handling and packaging practices, 2) potential alignment issues caused by the compromised thickness and shape of the wafer's edge, and 3) increased bowing as the wafer is thinned. These problems can lead to robotic handling problems and unreproducible wafer cassette positioning. In addition, 4) silicon fragments can dislodge from the sharp edge of the wafer and re-deposit in sensitive device structure areas, and 5) the sharp edge of a thinned wafer provides the most likely location for cracking to begin, which will eventually lead to wafer breakage.

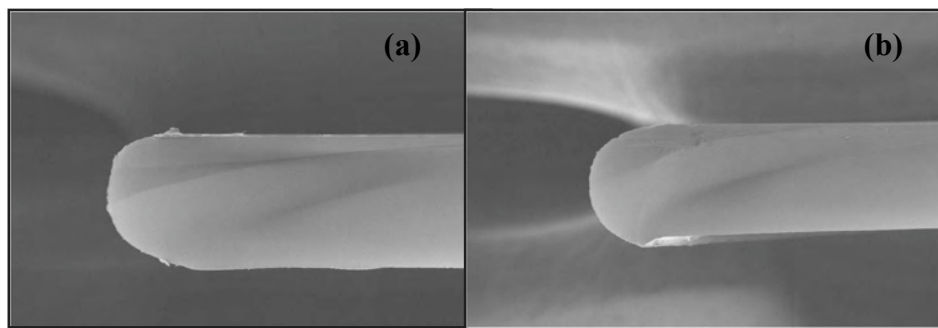


Fig. 9. Wafer with TALON Wrap™ edge wrap (silicon wafer edge with etch protective coating). a. Before KOH etch. b. After KOH etch.

The advantages of fully encapsulating the wafer (Figure 9a and b) during the etch process include: 1) wafer stability is increased, 2) less wafer breakage occurs during handling and packaging, 3) downstream wafer alignment is no longer a problem, as the wafer's edge and thickness have not been compromised, 4) wafer bowing is reduced due to the added

support of the edge, 5) the potential for silicon fragments to break free from the knife edge is eliminated, and 6) potential cracking at the wafer's edge is eliminated.

3. CONCLUSION

Primer compositions were developed to promote adhesion of the etch protective coating for both front-side and rough back-side applications. Primer solutions exhibit extraordinary shelf life. Hydrolysis of primer solutions was successfully monitored by use of gas chromatography. The fastest rate of hydrolysis was observed for primer solutions made with an acid, as hydrolysis was completed within a day of making the primer. Although, it took several weeks for primer solutions stored at room temperature to complete the hydrolysis, primer solutions performed as soon as they were manufactured, that is, no standing time was required. The slowest rate of hydrolysis was obtained for primer solutions stored under refrigerated conditions. No standing time was required for the mentioned primer formulations to deliver successful performance during extended hours of wet etching. Reported primer compositions were specifically tailored to accommodate the TALON Wrap™ process. Only one coat of primer solution was sufficient to promote adhesion of ProTEK™ coating during the TALON Wrap™ process. No film lifting or peeling was observed during extended hours (≥ 10 hr) of hot KOH wet etching with edge wrapped. In conclusion, enhanced throughput realized by an increase in the processing rate from 8 wafers/hour to 25 wafers/hour was achieved by combining the robust primer material with an advanced process and new technology.

4. ACKNOWLEDGMENTS

The authors wish to thank the following people at Brewer Science: B. Davis for GC data; S. Gibbons and R. Trichur, Applications Engineer for their help in conducting customers' demonstrations; C. Frank, J. Woodson, D. Guerrero and P. Allen for their expert comments in reviewing this paper; and M. Daily for his helpful discussions. Also, JDM would like to extend her thanks to A. Shen, formerly of Brewer Science, Inc. (now at DuPont Chemicals), for GC method development.

REFERENCES

1. E. P. Plueddemann, "Silane coupling agents," Plenum Press, New York, 1982
2. C. Li, K.A. Ruben, T.D. Flaim, "Spin-on protective coatings for wet-etch processing of microelectronic substrates," U.S. Patent Application No. 20050158538, July 21, 2005
3. G. J. Brand, P. Allen, R. Trichur, "Device for coating the outer edge of a substrate during microelectronic manufacturing," International Patent Application No. WO06071363A2, July 6, 2006