

remove the residue, however, at 180 sec. (3 min.) removal is complete (FIG. 4d). Had values above a pH=6 have been tested, they would have resulted in little or no change in residue appearance for the identified exposure times.

[0034] A characteristic beveling of the edge where the hard mask and side wall meet is observed in the exposure times of 180 sec. (3 min.) (FIGS. 4b, 4d and 4f), but does not appear as pronounced in the 45 second exposure (see FIGS. 4a, 4c, and 4e). Since the hard mask is composed of thermal oxide (see FIG. 2), it stands to reason that effects may exist from the ionized fluorine, especially for longer periods (i.e., 180sec.). In observing 180 sec. (3 min.) at pH 5.1 and 5.5 (FIGS. 4b and 4d, respectively), it is seen that a slight outline forming at the edge indicates that there may be some recession or attack occurring here. However, at the reduced exposure time of 45 sec. and pH 5.1 (FIG. 4a), the edge appears to be very straight with little or no hard mask etch (beveling). This beveling or edge attack requires cross-section analysis to determine the exact effects that exist.

[0035] A closer look at the oxide mask condition upon exposure to the invention with an approximate pH=5 at times of 45 sec. and 180 sec. suggests that mask removal is occurring with time. TEM analysis is used to conclude this phenomena by cross-section sample preparation. A FEI Strata Dual-Beam 235 FIB-SEM (focused ion beam-scanning electron microscope) was used to prepare TEM samples. Samples were coated with approximately 300 Å of chromium (Cr) in a Denton Hi-Res 100 sputter coater, then coated with a thin layer of epoxy, and an additional 300 Å of Cr to planarize and protect the sample from ion beam damage and provide a conductive sample surface. TEM samples were prepared using the AutoTEM software built into the FIB-SEM. A 1 µm layer of platinum was deposited over the area where the sample was made via ion-assisted deposition using the gas injection system on the FIB-SEM as part of the AutoTEM routine. The slices were lifted out and placed on a conductive web and transferred to acquire TEM images using a JEOL 2010F field emission gun operated at an accelerating voltage 200 keV. Conventional TEM images were recorded using a Gatan multi-scan digital camera (Model MSC794). Results on prepared samples indicates that a 45 second exposure still maintains a 47 nm (approximately 500 Å) thickness of SiO₂, whereas at a 180 second exposure the SiO₂ layer appears to be completely gone, as shown by reference to FIGS. 5a and 5b. The TEM photos shown in FIG. 5a are cross section analyses for patterned wafer exposure produced according to the invention with approximately pH=5 at times of 45 sec. and 180 sec. (3 min.) as a determination of edge bevel (hard mask attack). The representations of FIGS. 5a and 5b indicate that the longer time exposure of 180 sec. (3 min.) (FIG. 5b) results in thermal oxide (hard mask) removal.

[0036] Performance of the invention has been demonstrated to be sensitive with pH and performs in the range of 5-5.5, depending upon the process time and potentially, the tool. The post-etch residue break-up and removal may involve particulate generation as observed in the SEM photos in FIGS. 4a-4f (pH=5.01, granular appearance). These particles may have a tendency to redeposit and cause irregularities in the device topography and directly cause failure in its performance. Small particles attached to a substrate surface are bound by capillary adhesion energy. This energy can be reduced by decreasing the energy at the

solid-liquid interface (contact angle) through surface tension reduction. It is therefore important to ensure that good wetting (i.e., low surface tension and contact angle) is maintained throughout removal and rinsing, such that any particle generation is easily rinsed away. FIG. 6 depicts the change in surface tension of various surfactant additions to the invention formulation as it is mixed (rinsed) with DI water. Shown are surface tension changes upon mixing with different surfactants versus reference (no surfactant). Mixture of a hydrocarbon and fluorocarbon exhibits synergism, indicated by the best reduction in surface tension over the range of complete rinsing.

[0037] Reduction of both surface tension and contact angle can be achieved by mixing surface active agents. It is known that hydrocarbon surfactants (HC Surf) are effective at the liquid-solid interface (contact angle) while fluorocarbon surfactants (FC Surf) are best used for air-liquid interactions (surface tension). These systems were tested neat (reference) and in mixtures within the invention while mixing with DI water (rinsing effect). Care was taken for aqueous systems of high solids to prevent triggering the phenomena of salting out. The differences between HC Surf and FC Surf chemistries in a neat form is significant. The HC Surf offers a moderate plunge in surface tension yet maintains it over a wide range while the FC Surf exhibits a more dramatic reduction but is lost with dilution. Tests were performed by surface tension using a Fisher Scientific Tensiometer 21 with NBS standards. The best is achieved with mixtures of both (Surf Mix) to give good reduction over a prolonged mixing range to near complete rinsing with DI Water as illustrated by FIG. 6.

[0038] The invention is desired for use in spray tooling which are common to wafer fabrication areas. Chemistries which are successful in such tools must exhibit low foam character. Foaming capacity was tested on the surfactant mixture using Draves foam-height measurement techniques. The method involves a specific volume of analyte, normally 50 milliliters (ml), inserted into a 100 ml size graduated cylinder with cap. The cylinder is capped and shaken for a specific period of time, normally 15-30 sec., and immediately set onto a flat surface while observing the numeric gradations, which are superimposed onto the liquid. The measurement of foam height over the liquid level, in units of ml, are recorded within 5-10 sec. from shaking. The foam height may also be measured at increments of time extending from shaking, normally at 1 min. intervals. Since the interest in this invention is the level of foam generated in a spray tool, the foam height is measured within 5-10 sec. of shaking. Values of foam height for a range of surfactants and mixtures are reported in Table 1.

TABLE 1

Surfactant	Concentration (% w/w)	Foam Height (ml)
Zonyl® FSO-100	0.01-0.05	5-10
Plurofac® SL-92	0.1-0.3	25-30
Pluronic® 17B	0.1-0.3	<2*
Zonyl® FSO-100 & Pluronic® 17B	0.05-0.1	<5

*Note:

Solution concentrations >0.1 exhibit emulsion character.

[0039] The data in FIG. 6 and in Table 1, it is observed that a mixture of surfactants Zonyl® FSO-100 and Pluronic®