The Mechanism of Haze and Defectivity Reduction in a New Generation of High Performance Silicon Final Polishing Slurries

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Abstract The mechanism of haze reduction during silicon polishing using a new generation of additives has been explored. These additives are thought to decrease haze by adsorbing to the wafer surface and increasing the activation energy of the reaction between the silanolates on the silica particle surface with the surface silicon. This leads to greater selectivity between the peaks and valleys resulting in a net decrease in surface roughness.

Introduction Silicon substrates have been polished with high pH, silica based slurries for many years.[1-4] There have been numerous reports of using water soluble polymers to improve the surface quality of polished silicon wafers.[5-8] However, the introduction of ever-smaller features for advanced IC devices is driving the demand for slurries that result in improved surface quality. In this study, we will discuss a novel approach for reducing the particle defects and haze on silicon wafers. Such slurries can polish silicon surfaces to haze values below 0.030 ppm while maintaining removal rates of over 900 Å/min. This can enable a reduction in polishing time vs. commercially prevalent slurries and lead to lower slurry usage that can translate directly into a lower cost per wafer while yielding wafers with a superior surface finish.

Experimental 8" diameter, p^- boron doped, (100) silicon wafers were obtained from Silicon Valley Microelectronics. Wafers were polished on an IPEC Planar 472 at various down forces, table speeds and slurry flow rates. Removal rates were determined by weight differences to the nearest 0.00001g. The surface finish was analyzed with a Veeco D5000 AFM using a 5x5 μm spot size and a Wyko Veeco NT3300 white light interferometer. pH was measured with an Accumet Ap61 meter. Formulations were prepared by mixing colloidal silica under high shear with the appropriate chemical additives. Haze and defectivity (DCO and DCN) were measured via a KLA-Tencor SP1 TBI. Viscosities were determined using an Ubbelohde capillary viscometer held in a constant temperature bath at 25 ^{o}C.

Discussion Haze is a measure of the light scattered off of a surface. Lower roughness translates into less scattered light and a lower haze. Residual particles scatter light and also increase haze. Typical haze values are less than 0.1 ppm in the narrow normal channel for a highly polished, reflective surface. It is possible to add certain agents that adsorb to the silicon wafer to form a steric barrier which requires energy for the particles to penetrate and therefore reduces the removal rate. We believe that the removal mechanism for polishing silicon wafers with silica involves the interfacial nucleophilic attack of the silanolates on the silicon atoms on the surface of the wafer. Evidence includes a correlation between the silica zeta potential, which is related to the silanolate active site concentration, and the removal rate as well as dynamic light scattering data suggesting transetherification of the silicate formed onto the particle surface.[9] By controlling the hydrophilic/hydrophobic nature of the additives and their concentrations, it is possible to trade off removal rate for haze when added to silica-based silicon polishing formulations. Figure I shows the relationship by varying the concentration of a typical additive. Such additives may also facilitate the removal of particles during post-CMP cleaning.

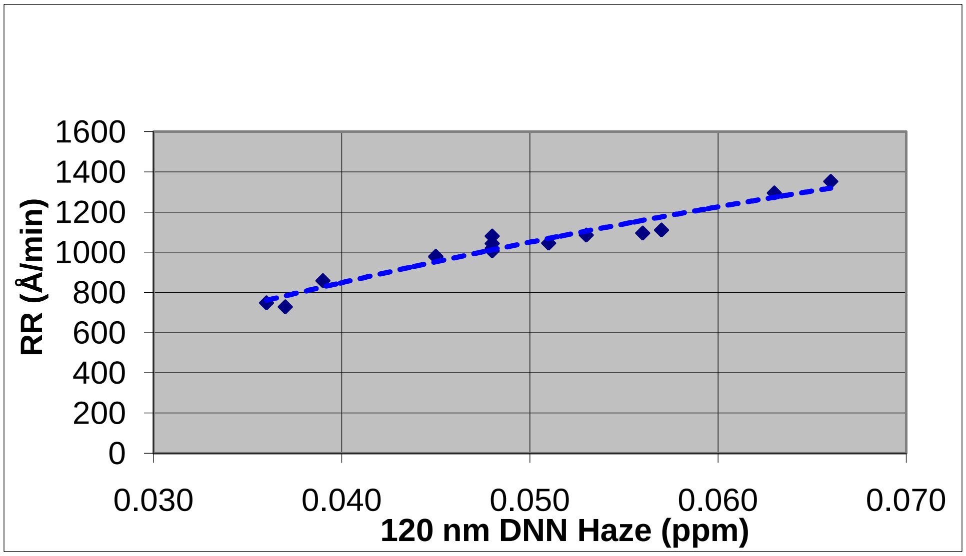

Figure I. The relationship between removal rate and haze in CMC slurries.

Figure II shows that the viscosity is unaffected by the addition of the haze controlling additive. This suggests that flow modification is not playing a significant role in haze reduction. On the other hand, the contact angle of the silicon wafer is affected by the additive. Before polishing, silicon wafers are somewhat hydrophilic due to the silicate passivation layer on the surface and have a contact angle with water of 35^o. The contact angle increases to 63^o when the wafer is polished with high pH silica alone due to the removal of the silicate exposing a hydophobic surface with Si-H groups which are hydrolyzed to silanols.[10] The addition of cleaning additives and haze reduction additives reduces the contact angle to 9^o and 5^o, respectively (Figure III). The significantly increased hydrophilicity of the wafers is evidence for adsorbtion of these additives to the silicon wafer surface.

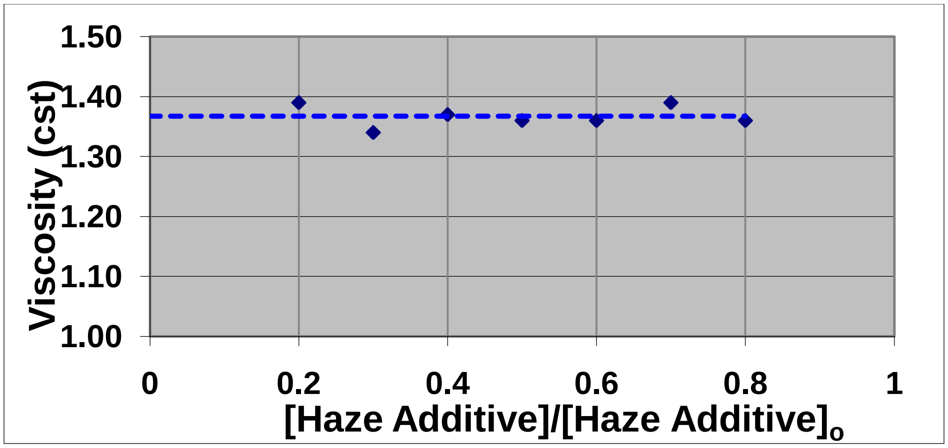

Figure II. The effect of additive concentration on the slurry viscosity.

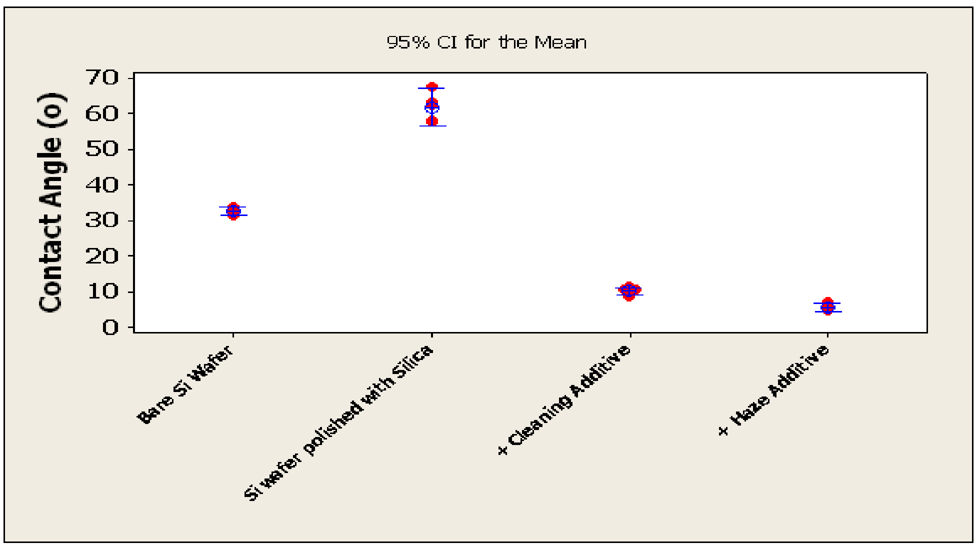

Figure III. The contact angle of silicon before polishing and after polishing with various silica slurries.

In an effort to understand the role of these additives, the surface roughness was studied by AFM and white light interferometry. Teichert[11] and subsequent authors[6-8, 12, 13] have shown that haze may be related to surface roughness. In our system, as the additive level increases from [haze additive]/[haze additive]$_o$ from 0.50 to 0.81 the AFM R_a decreases from 0.8 to 0.5 Å. Although suggestive, we were concerned that this change might not be meaningful. We had observed that certain amines will increase haze as their concentration increases. Although the amine used in this study would not be used in a final polish slurry composition due to the critical nature of haze in the silicon wafer industry, it is still useful for gaining a mechanistic understanding of factors affecting haze. Figures IV and V show the effect of R_a by AFM (5x5 μM image) and white light interferometry (2x3 mm image) as the amine concentration is increased yielding an exponentially increasing haze as the surface roughness increases. This increased roughness occurs on both the submicron scale roughness measured by AFM as well as the 0.1-2.0 scales measured by Veeco. The largest scale can be considered microwaviness with a wavelength near 3 mm. As measured by DCO, the particle defects were not significantly different and thus we can eliminate the influence of residual particles on the scattered light.

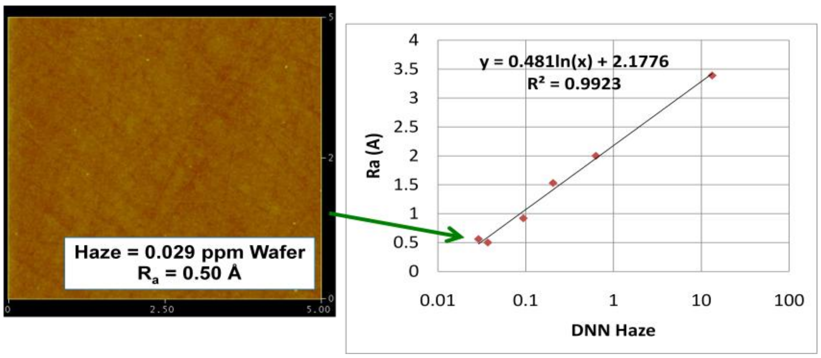

Figure IV. The effect of AFM roughness on the DNN haze.

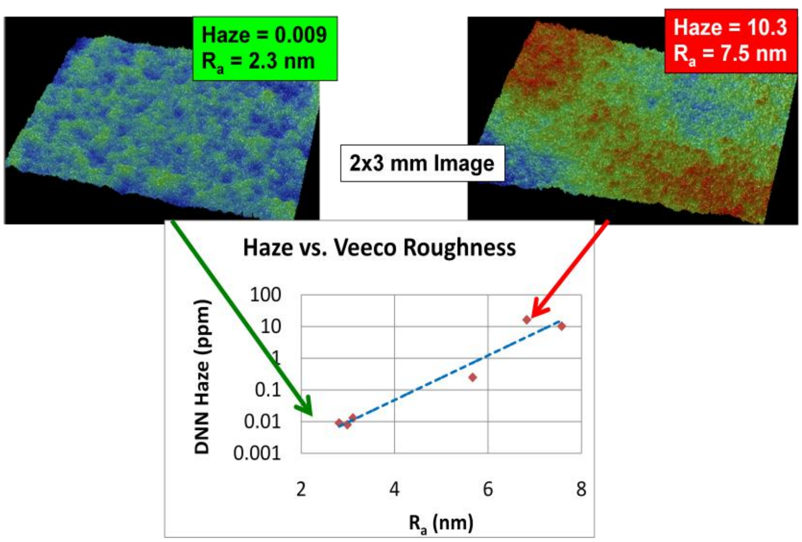

Figure V. The effect of Veeco roughness on the DNN haze.

The mechanism of defectivity reduction is thought to involve the adsorbtion of additive molecules to the silicon wafer surface. The additives are selected to create a steric barrier between the abrasive particles and the substrate. For haze reduction, the interaction energy between the additive and the silicon surface needs to be balanced such that the removal rate remains high on the peaks of the initially rough substrate where the kinetic energy of the particle is higher with locally higher pressures and shear rates while inhibiting polishing in the valleys. Lower roughness translates into less scattered light and a lower haze. Residual particles scatter light and also increase haze. We believe that residual particles can be reduced by creating a steric barrier between the particle and wafer that is sufficient to minimize covalent bonding between the substrate and particle. The proposed mechanism is displayed in Figure VI.

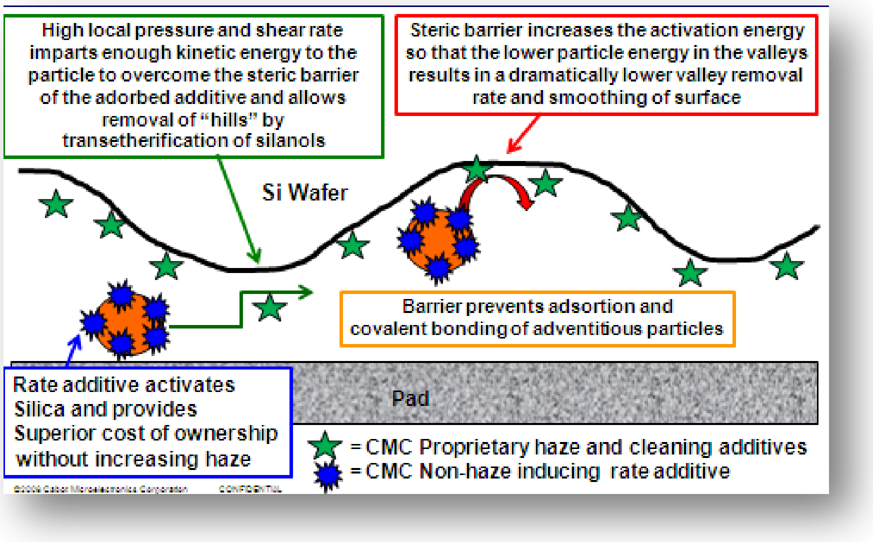

Figure VI. The mechanism of roughness/haze reduction.

The relative removal rates, haze and particle defectivity (DCO) are compared to a slurry that is considered to be one of the best on the market in Figure VII.

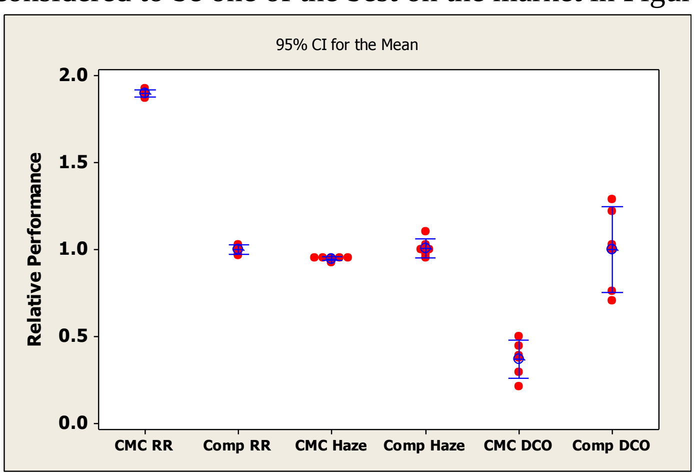

Figure VII. A comparison between a CMC slurry and a competitor's slurry.

Conclusions

The following conclusions can be drawn from this work.

1. Additives have been developed that reduce haze with a marginal effect on the removal rate.
2. Based on the contact angle data, the additives adsorb to the wafer surface.
3. An increase in surface roughness exponentially increases haze.

4. The additives may function by adsorbing to wafer surface and increasing the activation energy of the particle/surface reaction therefore enabling higher removal rates on the high spots and reducing the rate in the valleys, thus resulting in a smoother surface.
5. CMC's new generation of haze additives enables world class haze and defectivity.

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