# Reduced Zeta Potential Through Use of Cationic Adhesion Promoter for Improved Resist Process Performance and Minimizing Material Consumption

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## ABSTRACT

This paper presents the results of a non-HMDS (non-silane) adhesion promoter that was used to reduce the zeta potential for very thin (proprietary) polymer on silicon. By reducing the zeta potential, as measured by the minimum sample required to fully coat a wafer, the amount of polymer required to coat silicon substrates was significantly reduced in the manufacture of X-ray windows used for high transmission of low-energy X-rays. Moreover, this approach used aqueous based adhesion promoter described as a cationic surface active agent that has been shown to improve adhesion of photoresists (positive, negative, epoxy [SU8], e-beam and dry film). As well as reducing the amount of polymer required to coat substrates, this aqueous adhesion promoter is non-hazardous, and contains non-volatile solvents.

**Keywords:** adhesion promoter, reduce resist consumption, zeta potential, non-hazardous, green manufacturing

## 1. INTRODUCTION

Photoresists, polyimide, and other proprietary polymer emulsions have seen a rapid increase in usage recently due to the diversification in their applications for use in semiconductor devices, optical components, biomedical membrane manufacturing, and alpha ray shielding of semiconductors. In this paper, the name ‘polymer’ will be used to encompass all types of polymeric emulsion systems, both photoactive and non photoactive. With increasingly novel applications, the associated costs of manufacturing these highly specific niche polymer films have dramatically increased. In order to reduce manufacturing costs, there is a clear need to reduce the amount of polymer that is needed to spin coat a wafer or similar substrate.

### 1.1 Objectives

The desire to reduce resist consumption and reduce costs is not new, and has included use of solvents “pre-wet” steps just prior to the polymer spin coat. This technique reduces the zeta potential by introducing a solvent which is less costly than the polymer. However, the hazardous nature of these solvents and their disposal requirements again add unwanted manufacturing costs. This paper presents a novel approach to reduce the polymer consumption by reducing the zeta potential using an environmentally safe, non-hazardous, adhesion promoter / priming agent: SurPass 3000*

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* Proprietary photoresist adhesion promoter / priming agent manufactured by DisChem , Inc. Ridgway, PA USA
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## 1.2 Historical Relevance of Adhesion Promoters in Semiconductor Manufacturing

Successful microlithography requires that the photoresist be sufficiently adhered to the substrate to insure the integrity of lithographic structures throughout all stages of processing. Adhesion failure is characterized by up-lifting, peeling, pitting, or wash-off of the photoresist from the substrate during processing. Causes of photoresist adhesion failure include: chemical and thermal changes in the photoresist, out-gassing of decomposed photoactive compounds from the resist, thermal expansion, and contraction of the substrate, and insufficient substrate surface energy to maintain adequate adhesion between the substrate and lithographic features during processing. SurPass was developed by DisChem (Ridgway, PA USA) to address the specific causes of photoresist adhesion and improve overall resist coating in photolithographic processing. In addition to promoting adhesion, SurPass modifies the available surface energy and provides improved coating flow and uniformity even where photoresist adhesion is not an issue. It is the ability of SurPass to reduce the zeta potential of the substrate, subsequently for reducing polymer consumption, that is the focus of this study.

## 1.3 Zeta potential

The zeta potential can be represented as a measure of the shearing that occurs when the polymer is spun onto any substrate. The determination of the zeta potential is indirect and is done via the measurement of the electrophoretic mobility [1]. Immediately next to the surface, there is a layer of ions that are strongly attracted to the solid surface and are immobile [2]. The classical methodology for determining the surface conductance and zeta potential for a given surface is to perform a linear regressing of data obtained by Laser Doppler Velicometry (LVM). Using this technique as it applies to a polymer coating a substrate is problematic. This paper, instead, presents the results from functional testing for zeta potential that was carried out with silicon wafers using a proprietary polymer. The zeta potential functional tests were compared for bare silicon wafers (untreated) versus silicon treated with SurPass, an aqueous, non-silane adhesion promotion. The magnitude of zeta potentials can be compared by measuring how large a surface area is covered when an amount of polymer, less than sufficient to completely cover the surface, is spun onto a wafer.

## 1.4 Methodology

If there is a large electrostatic interaction between the liquid and solid of a polymer emulsion, there is a layer of ions that are strongly attracted to the solid surface that will be immobilized [3]. This immobilization will slow down the spread of polymer, and if a small enough polymer sample is used, then the resulting final spread diameter will be a direst measure of the electric potential between the solid and liquid layers; the polymer and the substrate. The electro kinetic effects of the polymer liquid as it slides over the silicon substrates will be measured as a function of the spread. By keeping the spin speeds, polymer sample size, tool exhausts, and all other controllable factors constant, the only difference between the treated and non-treated substrates is the SurPass adhesion promotion treatment. Whenever the spread area was increased, the electro kinetic potential between the polymer and the substrate had been decreased.

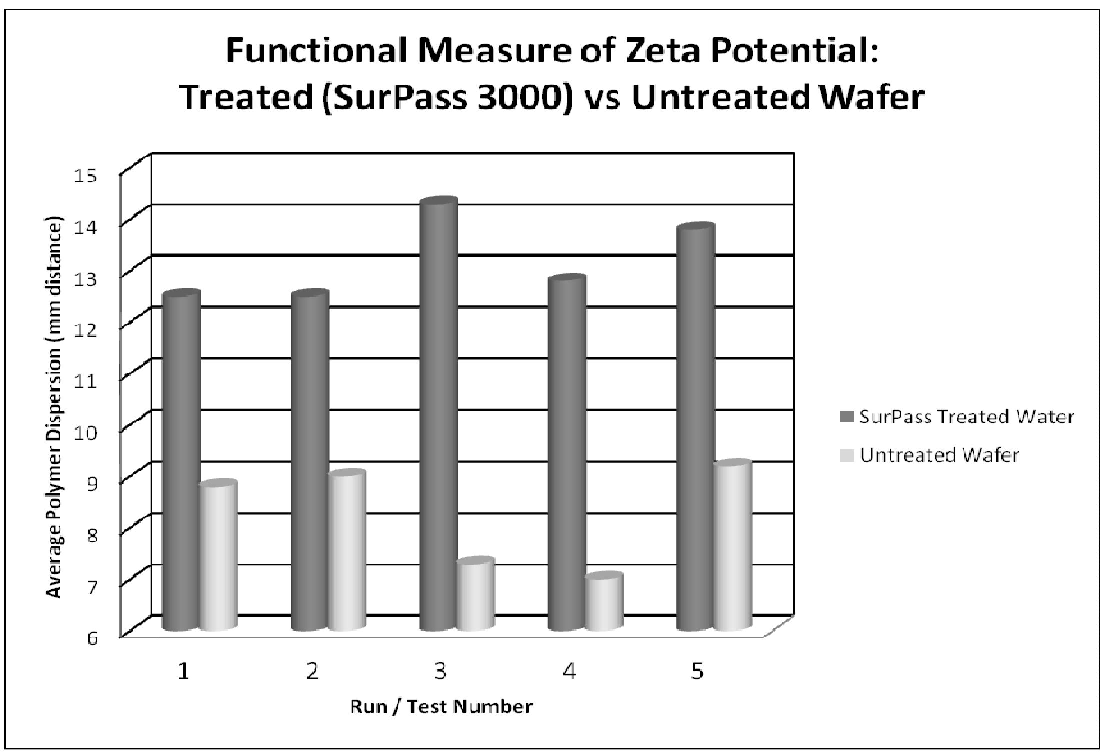
## 2. EXPERIMENTAL

Silicon wafers were primed by immersion in SurPass 3000 priming agent at room temperature for 30 seconds, then rinsed in DI water for 60 seconds and nitrogen blow dried. Bare silicon wafers were rinsed in DI water for 60 seconds and nitrogen blow dried. The primed and non-primed silicon wafers were coated with 0.067ml of proprietary polymer by manual dispensing at the center of each wafer in a static dispense using an AIO coat track. The spread and spin cast steps in the coating recipe were maintained at a constant 6000rpm using a 5000rpm/sec$^2$ acceleration. All coat bowl exhaust was turned off and the wafers were spun dry for 30 seconds. The wafers were baked at 90C for 90 seconds and the resulting size of polymer coverage on each wafer was measured using a visual metric and multiple measurements.

The SurPass-primed and non-primed wafers were processed at the same time and in a random fashion in order to minimize any uncontrollable tool and process errors.

## 3. DATA AND RESULTS

Quantative measurements of the polymer spread were made by measuring the five locations with the largest spread pattern. The spread patterns were not circular but resembled multifaceted stars. Measurements were taken bilaterally at the stars five outermost points. Because this was done visually, the measurements were repeated. An average was calculated for each run in the experiment and the results for SurPass treated wafers versus bare silicon wafers are shown below in Graph 1.



# 4. CONCLUSION

## 4.1 Reduction in polymer needed to coat wafer

The difference in size of the coated area of the SurPass treated wafers and those that were not treated was approximately 37%. This improvement in “spreadability”, when used as a functional test for zeta potential, can be used to evaluate several substrate types. Because all other conditions were kept constant, the improvement in coating performance can be attributed to SurPass exclusively. Silicon wafers that are coated with polymer without an adhesion promoter wound benefit from SurPass treatment and since it increases the coverage area by 37% a concomitant reduction in the amount of polymer that is needed to coat a wafer. This means an almost 40% reduction in the amount of chemical needed to coat a comparable wafer. It is hoped that further testing will be carried out to determine if this improvement is observed with other substrates such as metal or nitride thin films.

## 4.2 SurPass characteristics

SurPass is a waterborne cationic organic surface active agent designed to promote / enhance photoresist adhesion on a broad range of substrate materials. SurPass promotes photoresist adhesion through cationic interaction and modification of the substrate surface energy. Successful microlithography requires that the photoresist be sufficiently adhered to the substrate to insure the integrity of lithographic structures throughout all stages of processing. Adhesion failure, characterized by up-lifting, peeling, pitting or wash-off of the photoresist, thermal changes In the photoresist, out-gassing of decomposed photoactive compounds from the resist, thermal expansion and contraction of the substrate and lithographic features during processing. SurPass was developed by DisChem (Ridgeway, PA USA) to address the specific causes of photoresist adhesion and improve overall resist coating in photolithographic processing [4]. SurPass has shown[i] compatibility with most photoresist formulations, providing excellent adhesion when used with photoresist resins (DNQ/NOVOLAC), poly methyl methacrylate, poly methyl glutarimide (PMGI), epoxy based polymer (SU8), polyimide, electron beam and chemically amplified photoresist.

In addition to providing adhesion, SurPass modifies the available energy to provide a move uniform coating surface for improved resist flow. Evidence suggests the SurPass may be used in polymer processing to both improve performance and reduce material consumption through reduced Zeta potential. SurPass provides improved coating flow and uniformity even where photoresist adhesion is not an issue.

## 4.3 Safety and environmental impact

In addition to reducing the costs of materials (photoresists, etc) needed for manufacturing, by using a zeta potential reducing aqueous adhesion promoter such as SurPass, the cost of hazardous HMDS material disposal is eliminated because SurPass is non-hazardous. It has important implications and applications as companies attempt to incorporate green manufacturing by reducing the use of toxic chemicals, and promoting good corporate citizenship.

## REFERENCES

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