Introduction

When exposing on non-conductive substrates in electron beam lithography (EBL), a charge dissipating agent is required atop the resist layer to prevent charge accumulation on the surface to ensure proper shape placement and overall fidelity as like charges repel. Quaternary ammonium compounds (QAC) of the general structure NR4+ offer several advantages over traditional conductive polymer in EBL charge dissipation in that they remain permanently cationically charged independent of pH, are often water soluble, and offer extended shelf life at room temperature. Furthermore, quaternary ammonium compounds are highly tolerant of acids and oxidizers while demonstrating high dielectric capacity.

DisCharge H2O, a proprietary QAC water based formulation, is applied by spin coating, providing uniform conductive film for effective charge dissipation. The film remains soluble and can be removed by rinsing with either water or isopropyl alcohol.

An investigation of a novel QAC formulation, DisCharge H2O, was proven to show efficacy on a broad range of both positive and negative EBL resist materials. Furthermore, the thickness of the charge dissipation layer could be manipulated through modification of QAC content in the anti-charging agent.

1. Spin coat and pre-bake resist per protocol
2. Allow wafer/sample to cool to room temperature
3. Spin coat DisCharge H2O at 1000 rpm (film thickness of 40 nm). No soft bake required.
4. Remove DisCharge H2O film using one of the following methods:
   • Spin Rinse Removal: While spinning at 3000 RPM for 60 seconds, rinse with DI water or IPA
   • Sink Rinse Removal: Rinse with running DI water for 30-60 seconds
   • Solvent Rinse Removal: Rinse with steady stream of IPA for 30-60 seconds
5. Dry sample using N2 blow dry
6. Develop resist as normal

Process Description

<table>
<thead>
<tr>
<th>Sheet Resistance with Varying Thickness</th>
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<tr>
<td>Thickness [nm]</td>
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<td>0</td>
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Results and Discussion

Resist Compatibility and Charge Dissipation Efficacy

No charge accumulation is observed with the application of DisCharge H2O, whereas accumulation is observed without the application of a charge dissipating agent.

Key Learnings

DisCharge H2O Compatible EBL Resists
- CSAR 62 (positive resist containing poly (α-methylstyrene-co-chloromethacrylic acid methyl ester), plus an acid generator in anisole solvent)
- mr-PosEBR (acrylate-based positive resist in anisole solvent)
- ZEP520A (positive resist in anisole solvent)
- PMMA (poly(methyl methacrylate) positive resist)
- HSQ (hydrogen silsesquioxane negative inorganic resist)

DisCharge H2O Incompatible EBL Resists
- ma-N 2400 (negative organic novolak resist)

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Summary

An investigation of a novel QAC formulation, DisCharge H2O, was proven to show efficacy on a broad range of both positive and negative EBL resist materials. Furthermore, the electrical characterization of the DisCharge H2O film demonstrated the resistivity of the charge dissipation layer could be manipulated through modification of QAC content in the anti-charging agent.

Acknowledgements

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Charge dissipation by use of a novel aqueous based quaternary ammonium compound for use in electron beam lithography on non-conductive substrates

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ABSTRACT

Electron beam lithography (EBL) is commonly used for patterning at the nanoscale by way of a focused electron beam. This process can lead to charge accumulation on the surface of the resist when used in conjunction with non-conductive substrate materials, impacting lithographic quality producing egregious shape placement inaccuracies. Current practice requires the use of a deposited metal or conductive polymer film to facilitate charge dissipation at the surface. Such films are often unstable, incompatible and/or can be difficult to remove after exposure. This paper presents the findings of a study of a novel aqueous based quaternary ammonium compound for use in EBL for charge dissipation on non-conductive substrates. This compound was found to effectively prevent charge accumulation across a broad range of resist materials while remaining highly stable at room temperature and easily removed with deionized water or isopropanol after EBL exposure.

Keywords: electron beam lithography, charge dissipation, anti-charging agent

1. INTRODUCTION / MOTIVATION

Electron beam lithography (EBL) uses a highly focused beam of electrons to create nanoscale patterning on a broad range of substrates. When used on non-conductive substrates, including fused silica, quartz, PDMS, etc., a charge dissipating agent is required atop the resist material to prevent charge accumulation to ensure proper shape placement and prevent dielectric breakdown of the resist.

Existing technologies employ the use of conductive polymers or deposited metals to create a conductive film for dissipating the charge away from the surface of the resist. The available charge dissipation agents are often prohibitively expensive, increase process steps (i.e. vacuum metal deposition), are unstable and / or difficult to remove after exposure and development of the resist. Both current methods have known draw backs. Conductive polymers (polyelectrics) are prone to drifting pH, with conductivity diminished as the pH drifts beyond the optimum range. Precipitation of the polymers also occurs increasing the risk of contamination. As a result, polyelectrics are prone to a shorter shelf life and usually require refrigerated storage, an alcohol co-solvent and filtration prior to application. Evaporated metal films, usually 20-30 nm of Al, Au, and Cr are also used to create a conductive layer on the resist for charge dissipation. While highly effective, the evaporative metallization process can be very time consuming (up to several hours depending on the method) and require a wet chemical etch to remove the metal after EBL exposure.

A novel approach looked at the use of a class of conductive compounds quaternary ammonium compounds for EBL charge dissipation was investigated that offers the required conductive film properties. Quaternary ammonium
compounds (QAC) of the general structure NR₄⁺ offer several advantages over traditional conductive polymer in that they remain permanently cationically charged independent of pH, are often water soluble, and offer extended shelf life at room temperature. Furthermore, quaternary ammonium compounds are highly tolerant of acids and oxidizers while demonstrating high dielectric capacity.

A proprietary QAS water based formulation, DisCharge H2O[1], which is applied by spin coating and is readily removed by DI water or IPA rinsing, is studied here. The formulation was optimized for resist coating properties and to provide a 40 nm conductive film when applied at 1000 RPM. The film remains water soluble and can be removed by rinsing with either water or isopropyl alcohol.

2. EXPERIMENTAL

The study of the DisCharge H2O QAC formulation focused on two areas of investigation: 1) preventing charging effects and successful patterning on commonly used positive and negative EBL resist materials and 2) electrical characterization at varying QAC concentrations and film thicknesses.

2.1 Resist Compatibility and Charge Dissipation Efficacy

2.11 Resist Materials

Test slides of various non-conductive substrate materials including fused silica, quartz, and PDMS on bulk Si were coated with EBL resist. The following resist materials were used:

- CSAR 62 (Allresist GmbH [2]): positive EBL resist containing poly (α-methylstyrene-co-chloromethacrylic acid methyl ester), plus an acid generator in anisole solvent.
- m-PosEBR (Micro Resist Technology, GmbH [3]): positive tone acrylate-based positive resist in anisole solvent.
- ZEP520A (Zeon Corporation): positive EBL resist in anisole solvent.
- PMMA (MicroChem Corp. [4]): poly(methyl methacrylate) positive resist.
- HSQ (Dow): hydrogen silsesquioxane, an inorganic negative tone resist.
- ma-N 2400 (Micro Resist Technology, GmbH). Negative tone organic novolak EBL resist

2.12 Sample preparation: resist preparation, application and removal of anti-charging agent

Application and removal of the conductive DisCharge H2O film on the prepared test samples per the following protocol:

1. Spin coat and pre-bake resist per protocol.
2. Allow wafer / sample to cool to room temperature.
3. Spin coat DisCharge H2O at 1000 rpm to provide a film thickness of 40 nm. No soft bake is required. The DisCharge film remains tacky to the touch - avoid touching the film as it may smudge. Film should have gloss finish.
4. EBL Tool: Mount sample with grounding clip touching the surface of the sample. Expose desired pattern.
5. After resist exposure, remove the DisCharge film using one of the methods below:
   a. Spin Rinse Removal
      i. Mount wafer / sample in spinner and set for speed of 3000 RPM for 60 seconds
      ii. Initiate spin and rinse with generous amounts of DI water or IPA.
      iii. Spin dry or by using an N₂ blow dry.
   b. Sink Rinse Removal
      i. Firmly hold the sample and rinse with running DI water over a sink for 30-60 seconds.
      ii. Thoroughly dry the sample using an N₂ blow dry.
   c. Solvent Rinse Removal (IPA)
      i. Firmly hold the sample and rinse with a steady stream of isopropyl alcohol for 30-60 seconds over a beaker to capture solvent.
ii. Thoroughly dry the sample using an N₂ blow dry.

6. Develop resist as normal.

2.13 Resist Exposure and Development

Exposures were performed on various resist materials using an Elionix ELS-7500EX 50 keV. Test structures consist of 60 micron squares exposed at various doses using a 20 nm beam step (shot pitch) with 1 nA beam current. Experiments were performed at the University of Pennsylvania’s Singh Center for Nanotechnology Quattrone Nanofabrication Facility. Test sets were prepared for each of the EBL resist materials sited above to include same results with and without DisCharge anti-charging agent.

2.14 Results and Findings of Resist Compatibility and Charge Dissipation Efficacy

The following images provide evidence of efficacy for DisCharge H₂O acting as a charge dissipation agent in electron beam lithography:

300 nm PMMA 950 A4 / 1mm PDMS / bulk Si

Fig. 1: Without DisCharge H₂O: charge accumulation and sudden charge dissipation caused by exceeding the dielectric break down strength of the PDMS to Si substrate resulting in significant cracking of the resist.

Fig 2: WITH DisCharge H₂O: no charge accumulation, resulting in expected image with no damage to the PDMS.
300 nm mr-PosEBR on Glass Slide

Fig 3: Without DisCharge H2O: charge accumulation leading to poor shape fidelity of the contrast curve.

Fig 4: With DisCharge H2O: no charge accumulation is observed. The structure appears as expected. Crosslinking of the positive resist is especially observed at high doses.

200 nm ZEP520A of Glass Slide

Fig 5: Without DisCharge H2O: charge accumulation leading to poor shape fidelity of the contrast curve pattern.

Fig 6: With DisCharge H2O: no charge accumulation is observed. The structure appears as expected. Crosslinking of the ZEP520A resist is especially observed at high doses.
**300 nm CSAR62 on Glass Slide**

Fig 7: Without *DisCharge* H2O: charge accumulation leading to poor shape fidelity of the contrast curve.

Fig 8: With *DisCharge* H2O: no charge accumulation is observed. The structure appears as expected. Crosslinking of the CSAR62 resist is especially observed at high doses.

**HSQ on Fused Silica**

Fig. 9 With *DisCharge*: successful structure patterned. Structure would not have been possible with the use of a charge dissipation agent.
DisCharge H2O was found to be incompatible with this resist. Poor charge dissipation was occurred at standard concentration with chemical reactivity readily observed at higher concentrations (4X).

**Nanoscale Impact DisCharge on Tower Patterns**

Discharge efficacy was testing at the nanoscale using tower patterns in a dose matrix using 300 nm ZEP520A atop fused silica. The tower patterns consist of 300 nm line space patterns at various pattern densities. The results of this testing is shown below:

**ZEP520A 300 nm line space patterns atop fused silica**

![ZEP520A 300 nm line space patterns atop fused silica](image)

**Fig 10**: Without *DisCharge H2O*: charge accumulation resulting in poor shape fidelity of the tower pattern.

**Fig 11**: With *DisCharge H2O*: no charge accumulation is observed. The structures appear as expected.
2.2 Electrical Characterization at Varying QAC Concentrations and Film Thickness

A study was performed to examine the conductive properties of the DisCharge H2O film at containing varying concentrations of QAC. Samples were prepared containing QAC concentrations at 1X (standard DisCharge H2O formulation), 2X and 4X.

2.22 Spin curve profiles

The spin coat profiles were then prepared for all three sample groups to provide the following:
2.21 Manufacture of Four Point Probe Device

The electrical characterization of increasing film thickness was measured by creating a four point probe with four gold contact pads deposited on a fused silica substrate using the method described below:

1. AMI clean of 25mm² fused silica (four samples)
2. Spin on S1813 positive resist at 3000RPM
3. Soft bake 115°C
4. Write box pattern on Heidelberg DWL66+ (10mm WH, 50% filter, 200mW LP)
5. Develop MF319, 60s w/ manual agitation, water rinse, N2 dry
6. Deposit 50nm Au (Kurt J. Lesker PVD75, e-beam evaporator, 2 Å/s)
7. Liftoff with Microposit Remover 1165 (60°C w/ sonication)
8. Spin DisCharge at 1000, 2000, 3000, and 4000 RPM for each dilution
9. Ensuring that probes are contacting the Au pads, measure current and voltage with a four point probe. Four contact pads were deposited for each sample concentration for a total of 12 measurements.

Fig. 14: Design, Manufacture and Use of Four Point Probe

Box Pattern  Complete Sample  Using four point probe thin-sheet approximation: (t < probe spacing)
2.22 Calculation of Sheet Resistivity

Using the four point probe, sheet resistance was measured using the equation:

\[ \rho = \frac{\pi}{\ln(2)} \left( \frac{V}{I} \right) t = 4.532 \left( \frac{V}{I} \right) t \]

The data was used to create a graph shows that the averaged sheet resistivity.

![Sheet Resistance vs. Thickness](image)

Fig. 15

2.23 Results and Findings of Electrical Characterization at Varying QAC Concentrations and Film Thickness

The spin curves show a direct correlation between QAC concentration and the thickness of DisCharge H2O film with thickness doubling with each doubling of concentration. This pattern is consistent from application speed ranging from 1000 to 4000 RPM. Furthermore, resistivity is shown to increases proportionally to the thickness of the DisCharge H2O film.

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Fig. 16

3.0 CONCLUSIONS
Charge dissipation agents are required to perform EBL on non-conductive substrates to prevent charge accumulation of the resist. Failure to adequately dissipate the charge may lead to dielectric breakdown of the resist, poor shape fidelity and egregious shape placement. Conductive polymers or metal films are typically used for charge dissipation purpose is EBL but have known problems including a short shelf life of the polyelectric; difficulty in removal of the polymer / metal film after exposure; and extended process steps and time. An investigation of a novel QAC formulation, DisCharge H2O, was proven to show efficacy on a broad range of both positive and negative EBL resist materials. Furthermore, the electrical characterization of the DisCharge H2O film demonstrated the resistivity of the charge dissipation layer could be manipulated through modification of QAC content in the anti-charging agent.

ACKNOWLEDGEMENTS

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