

Development of Novel Purifiers with Appropriate Functional Groups Based on Solvent Polarities at Bulk Purification

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ABSTRACT

Weak-polar solvents like Propylene Glycol Monomethyl Ether Acetate (PGMEA) or Cyclohexanone (CHN) are used to dissolve hydrophobic photo-resist polymers, which are challenging for traditional cleaning methods such as distillation, ion-exchange resins service or water-washing processes. This paper investigated two novel surface modifications to see their effectiveness at metal removal and to understand the mechanism. The experiments yielded effective purification methods for metal reduction, focusing on solvent polarities based on Hansen Solubility Parameters (HSP) and developing optimal purification strategies.

INTRODUCTION

Today's chemical suppliers and their Original Equipment Manufacturers (OEMs) are feeling the pressure to reduce metal contamination from Integrated Device Manufacturers (IDMs) pushing the envelope with ever-smaller technology nodes. It's anticipated that each metal concentration should be controlled less than 10 ppt in advanced photoresists by 2018. Chemical manufacturers can manufacture ultra-pure solvents at single- or sub-ppt level; however, reaching the target specification dictated by the market is still a technical challenge because of the mutual interaction between metal contamination and additives. Actually, traditional methods of metals reduction such as distillation, ion-exchange resins service or water-washing processes need further improvement, particularly for polymer solutions. Also, weak-polar

solvents like PGMEA or CHN have recently been used to dissolve more hydrophobic photoresist polymers where current purification technology is inadequate. Under such situation, IDMs have occasionally faced unexpected cone defects and device performance deterioration derived from insufficient metal reduction in raw materials (Shown in Figure 1). Chemical companies continue to seek out innovative purification technology to achieve their challenging specifications.

In this paper, the metal removal efficiency of two tailored membrane technologies was investigated in actual photochemical solvents with different polarities such as Propylene Glycol Monomethyl Ether (PGME), PGMEA and CHN. The result proved that metal removal performance is highly dependent on solvent polarity based on Hansen Solubility Parameters. This analytical approach could bring us to excellent purification strategy.

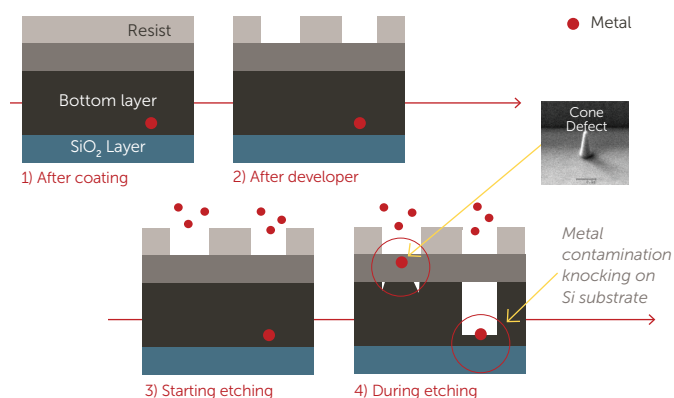


Figure 1. Illustration of metal contamination inducing defects on lithography process.

Experimental Set Up

The metal challenge solution was first made by adding 5 ppb of metal analytical standard, an oil-based standard Conostan® 21 plus Potassium (K), to the test solvent. Using the test stand shown in Figure 2, purification was conducted under steady flow by adjusting inlet pressure while monitoring the flow rate of 10 mL/min. Influent and effluent metal concentrations were measured using a standard ICP-MS analytical tool (Agilent 7800s). Each 47 mm coupon 2 ply from Protego® Plus, Entegris 10 nm rated nylon, two different kinds of purifiers called Purasol™ SP and SN were used for the test.

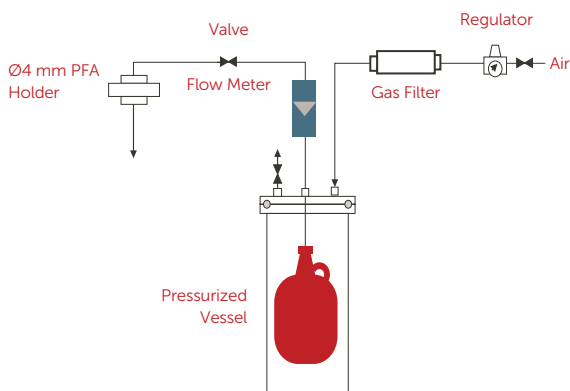


Figure 2. Test stand for metal challenge test.

Chemical Reaction Investigation

The soaking method was used to evaluate how much Purasol SN and Protego would cause chemical reaction in CHN. Used each sample of Optimizer-D format poured with CHN and extracted the solution one week later for GC-MS analysis (PerkinElmer Clarus® 500GC).

RESULTS AND DISCUSSION

Metal Reduction and its Metal Removal Mechanism in Lithography Solvents

The graph shown in Figure 3 illustrates that Fe removal capability depends on each solvent polarity. Purasol SP shows the best performance in PGME/PGMEA mixture, while Purasol SN shows better performance in PGMEA and CHN. Figure 4 demonstrates similar behavior in multi-metal removal in PGMEA/PGME.

Therefore, it can be interpreted that Purasol SP is effective in reducing metal contamination in more polar solvents such as PGME/PGMEA mixture, whereas Purasol SN is more suitable in less polar solvents such as PGMEA and CHN.¹

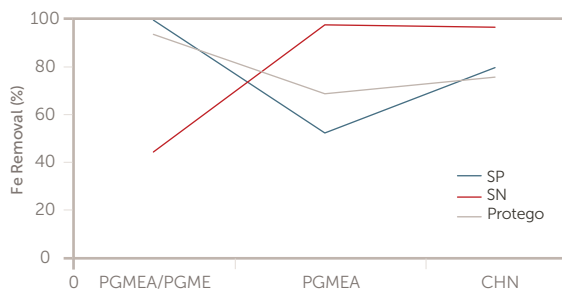


Figure 3. Fe removal performance dependency on each solvent polarity.[†]

[†]The data on other metals is not shown to see easily each performance.

Table 1. Recommendation and polarity for each solvent.

Solvent	Polarity ^{††}	Recommendation
PGME/PGMEA = (7.3)	80	Purasol SP
PGMEA	64	Purasol SN
CHN	32	Purasol SN

^{††}Calculated by $\sqrt{DH^2 + DP^2}$. dP stands for polarity and dH hydrogen bonding of HSP respectively.

Metal Removal Efficiency of Purasol SP and SN in PGMEA/PGME

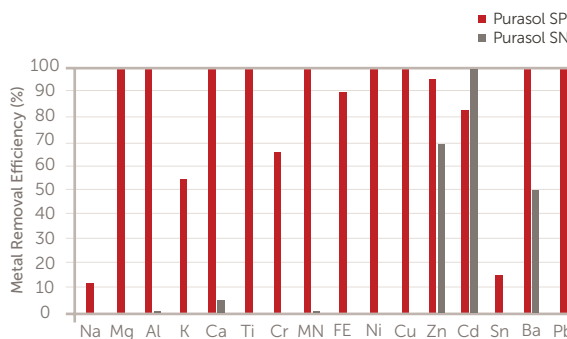


Figure 4. Multi-metal removal efficiency of Purasol SP and SN in PGMEA/PGME mixture.

Metal Reduction in Photochemical Solutions

The results shown in Figure 5 further illustrates that Purasol SN could work effectively in less polar solvents such as PGMEA with customer's photoresist polymer. As mentioned, in general it's the most challenging to reduce metal contamination in polymer solutions. However, this result may indicate the following assumption that additives can combines with metal contamination, especially transition metals to form aggregates as a core of those metals, which means that its polymer property will shift to much more hydrophilicity after aggregation even if they are hydrophobic property in nature. Therefore, this adsorption would occur under the same mechanism as PGMEA and CHN.

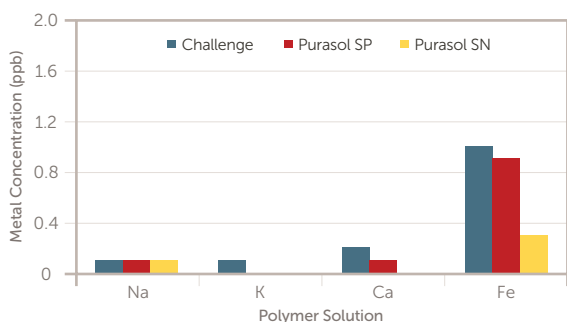


Figure 5. Metal removal testing in a photoresist polymer solution.^{†††}
^{†††}JSR provided this data.

Compatibility Study of Various Purifiers in Cyclohexanone

It is known that current Protego purifiers are not fully compatible with ketone solvents such as Cyclohexanone. The GC-MS shown in Figure 6 demonstrates that Protego purification media undergoes chemical reaction with CHN, producing undesirable by-products causing color change in solution from transparency to yellow (Figure 7). On the other hand, Purasol SN proves to be fully compatible with CHN with superior metal removal efficiency as shown in Figure 8. In addition, distillation is a common, yet costly practice to enhance solvent purity. Therefore, Purasol could be a cost effective alternative to distillation purification.

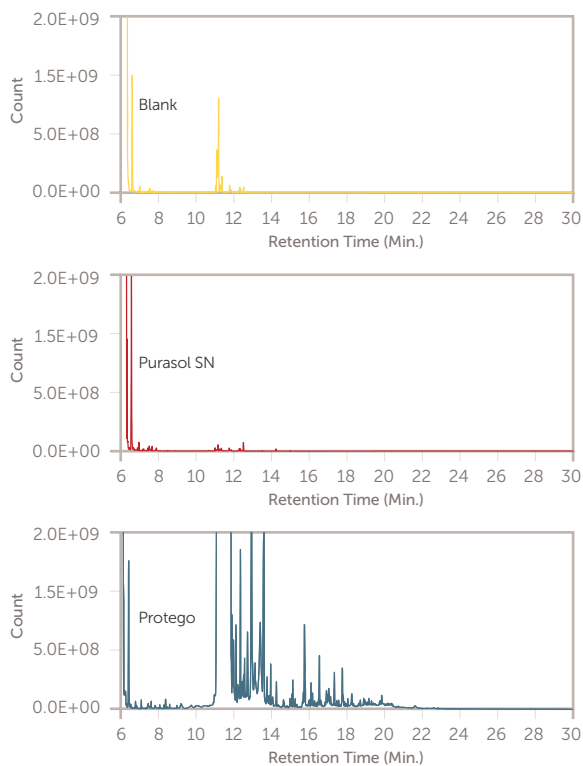


Figure 6. GC-MS chromatography (top: Blank; middle: Purasol SN; bottom: Protego Plus).

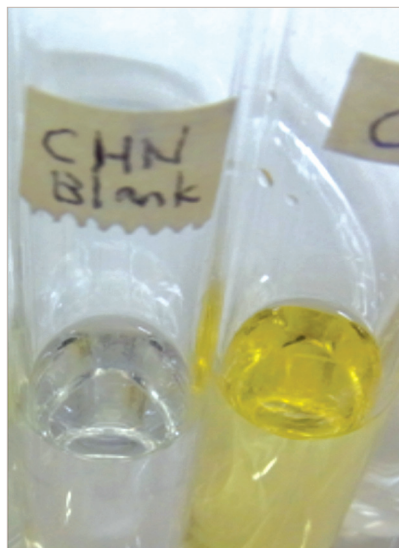


Figure 7. Discoloration of CHN (left: Blank; right: Protego after 1 week soaking).

Metal Removal Efficiency of Purasol SP in CHN

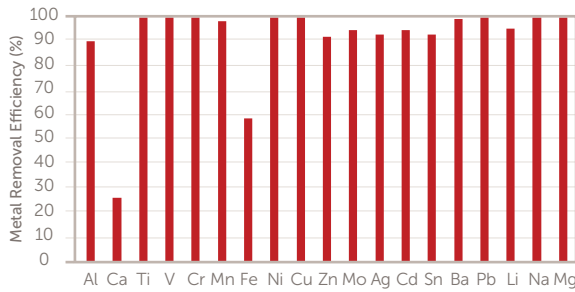


Figure 8. Multi-metal removal efficiency of Purasol SN in cyclohexanone.

CONCLUSION

It was found that solvent polarity plays a key role in metal removal performance. Entegris has developed two uniquely tailored purification technologies for total metal reduction in wide range of solvent polarities. Purasol SP was shown to effectively reduce metal contamination in highly polar solvents such as 70:30 mixtures of PGME and PGMEA, while Purasol SN could be effective in less polar solvents such as PGMEA and CHN.

In addition, Purasol SN is more effective in removing metal contamination in PGMEA-based polymer solutions. Although PGMEA and CHN have been employed recently to dissolve resist polymers, they are inadequate and/or not fully compatible with current purification needs. Therefore Purasol purifiers provide a much needed solution to the technical challenges of metal contamination.

This paper was first presented at the 2017 SPIE Advanced Lithography + Patterning conference.

References

¹ Israelachvili, J.N., *Intermolecular and Surface Forces, Second Edition*, Mac Graw Hill Education Co., Ltd., 30 (1991).

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