Effects of Cleaning on NIL Templates: Surface Roughness, CD and Pattern Integrity

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ABSTRACT

Nano-Imprint Lithography (NIL) is considered a promising alternative to optical lithography for technology nodes at 22nm hp and beyond. Compared to other advanced and complex lithography methods, NIL processing is simple and inexpensive making it a widely accepted technology for pattern media and a potential cost effective alternative for CMOS applications. During the NIL process, the template comes into direct contact with the resist on the substrate and consequently template cleanliness plays a decisive role in imprinted substrate quality. Furthermore, if the template has any form of a defect such as resist residue, stains, particles, surface scratches, chipping and bumping etc. it can lead to poor quality imprints, low yield and throughput decreases.

The latest ITRS roadmap has stringent CD, CD uniformity, surface roughness and defect control requirements for NIL templates. Any template cleaning process that is adopted must be able to remove defects while maintaining the critical parameters outlined by the ITRS. Aggressive chemistries (such as NH_4OH or SC1 (NH_4OH+H_2O_2+DI) and strong physical force treatments (such as MegaSonic & Binary Sprays) may cause damage to the template if not optimized. This paper presents the cleaning chemical effects on template surface roughness and CD at varying concentrations. The effect of physical force cleaning on fragile and sensitive pattern features is also presented. Particle & imprint resist removal efficacy at different process conditions is compared.

Keywords: NIL template cleaning, feature damage, roughness, CD change, MegaSonic, pattern damage, SC1, NH_4OH

1. INTRODUCTION

Hard Template Nano-Imprint Lithography (NIL) such as; Jet and Flash Imprint Lithography (J-FIL™) and Thermal Nano-Imprint techniques, is considered a cost-effective alternative to Next Generation Lithography [1,2] for some devices and geometries. The potential for extreme accuracy and small-feature resolution makes NIL fabrication ideally suited for the repetitive pattern features found in Flash memory and Hard-Disk Drive (HDD) Patterned Media, i.e. Discrete Track Media (DTM) and Bit Patterned Media (BPM).

The NIL high-resolution process is a 1:1 pattern transfer technology that utilizes direct contact of the template with the resist to produce the imprint. A single defect or particle on the template can be repeatedly imprinted leading to high yield loss. Depending on the soft defect source, there is a potential to remove or self-clean the template during the imprinting process itself. However, self-cleaning cannot be considered a robust, repeatable cleaning methodology. Repeated contact of the template and the resist during the NIL process, presents unique cleanliness issues that need to be addressed [3,4]. UV cured resist residue on the template can produce subsequent poor quality imprints. Frequent template inspection would ensure that the template is particle and defect-free however, the cost to remove the template from production and inspect would far outweigh the benefits. A quick, effective cleaning process is needed that can remove contamination while completely preserving the NIL template surface.

NIL templates for semiconductor devices (i.e. Flash memory) have been standardized across several characteristics. Most common masters and templates use a 6025 fused-quartz plate with the pattern on a slightly raised "mesa". The "mesa" is similar to those on the previously utilized 65mm square template. Patterned Media (PM) templates commonly utilize a 150mm or smaller Fused Silica wafer with and without thin Cr (~15nm) surface layers. As with the semiconductor device NIL templates, the Silica wafers utilize similarly patterned "mesa" areas.

Some of the most advanced cleaning processes have been developed to meet stringent mask integrity requirements of current and future EUVL and 193i lithography [5-7]. Developed on optical 4:1 reticles with different material composition, these advanced cleaning processes are not directly transferrable to a NIL template cleaning process. The

Photomask Technology 2011, edited by Wilhelm Maurer, Frank E. Abboud,
Proc. of SPIE Vol. 8166, 81662P · © 2011 SPIE · CCC code: 0277-786X/11/$18 · doi: 10.1117/12.898649

smaller geometries found on the NIL hard templates, require different chemistries and in some case less physical force to effectively clean and maintain template integrity. For example, Fused Silica templates in 6025 or wafer format need to be stripped and cleaned with different priorities in mind:

- NIL patterns can have relatively a higher aspect ratio compared to photomasks;
- NIL template surface materials are generally only quartz or chrome;
- Physical cleaning forces must be understood and controlled to prevent pattern damage;

Overly aggressive cleaning chemistries can cause surface roughness and/or CD change. Surface roughness increases the risk of post-imprint defects adhering to the template surface. CD change can eventually result in a shift of the imprinted pattern out-of-specification. Understanding cleaning induced roughness and CD change is essential for accurate estimation of template lifetime.

To-date, there are no reports on NIL template cleaning to address potential erosion of the quartz surface from various chemicals. Earlier HamaTech published a paper on the effect of cleaning on imprinted wafer CD, however such wafer imprinting tests contain large error margins making it difficult to accurately predict CD loss [11]. In this paper, the effects of wet cleaning chemistry and concentration on surface roughness and CD changes are examined for NIL templates. The potential physical force damage related to MegaSonic and Binary spray treatment on fragile and sensitive pattern features is determined and presented in this paper. An estimated number of wet cleans is established that can be sustained by a template during its lifetime without any loss to surface integrity

2. EXPERIMENTAL

2.1 Materials & Methods

65mm quartz templates were intentionally contaminated through wafer imprinting and the residual imprint resist was removed using a Process of Record (POR) cleaning cycle. Verification of the imprint resist removal process was accomplished using a Lasertec M2351 particle inspection tool to inspect the cleaned templates. Surface roughness was studied on dry etched quartz blank samples. The quartz blank samples were inspected using AFM (SII L-trace) before and after 3x and 20x cleaning cycles with POR and at a higher ammonia concentration than the POR (> POR). Patterned quartz templates were used to study CD (Critical Dimension) change and Pattern Damage. CD measurements were done on Advantest LWM-9000 CD-SEM tool. The pattern line-space features were 24nm wide and 100nm high (aspect ratio 4:1). The pattern was inspected in predefined locations in a 9x9 array with individual inspection area of 3µm × 3µm for all 81 locations. Chrome-coated templates were used in metal damage studies. Chrome thickness was measured before and after POR cleaning. Particle Removal Efficiency (PRE) was studied by depositing variously sized SiN and SiO_2 particles on quartz blanks. Defect/particle counts taken before and after cleaning from inspections on the Lasertec M2351, were used to calculate PRE performance. A summary of the sample types, respective experiments and conditions are described in Table 1 below.

Evaluation	Sample Type	Process Cycles	NH_4OH Concentration
Imprint resist removal	Imprinted 65mm Qz template	1x	POR
Surface Roughness	Qz blank	20x	> POR / POR
CD Change	Patterned Qz template	20x	> POR / POR
Pattern Damage		20x	POR
PRE	SiO_2 deposited Qz blanks	1x	POR
	SiN deposited Qz blanks	1x	> POR / POR
Cr Damage	Cr/Qz Template	1x	POR

Table 1: Summary of performed experiments and conditions.

2.3 Cleaning Procedure

All Cleaning was performed on, the SUSS MaskTrack TeraPure. MaskTrack TeraPure was designed to address the specific requirement of advanced imprint template cleaning. In initial step in the POR cleaning process the surface was properly wetted before it is actually cleaned. Conventional surface conditioning techniques were accomplished using dry methods such as 172nm VUV, requiring a separate chamber and controlled environment. For this experiment, however, UV photon energy and DI-water was used to complete surface conditioning step under atmospheric conditions. Surface conditioning was followed by acid-free organic removal using photolyzed DI-O_3 (Ozone water), a process developed by HamaTech to remove UV-cured imprint material residue from a NIL template. A SC1 (NH_4OH+H_2O_2+H_2O) solution

was used for particle removal along with advanced MegaSonics and binary spray droplet treatment ensuring pattern integrity of the fragile features. The process was concluded with an ultra pure DI-water rinse and dry (Figure 1).

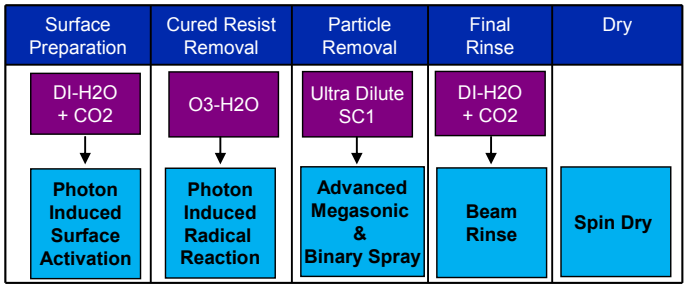

Fig. 1: Flow chart showing details of Process of Record (POR) cleaning steps sequence used for template cleaning process.

3. RESULTS & DISCUSSION

3.1 Imprint Material Removal

The NIL hard templates were intentionally contaminated with imprint resist material and then cleaned with the acid free POR process. Figure 2 presents the defect maps for two templates after cleaning with the POR.

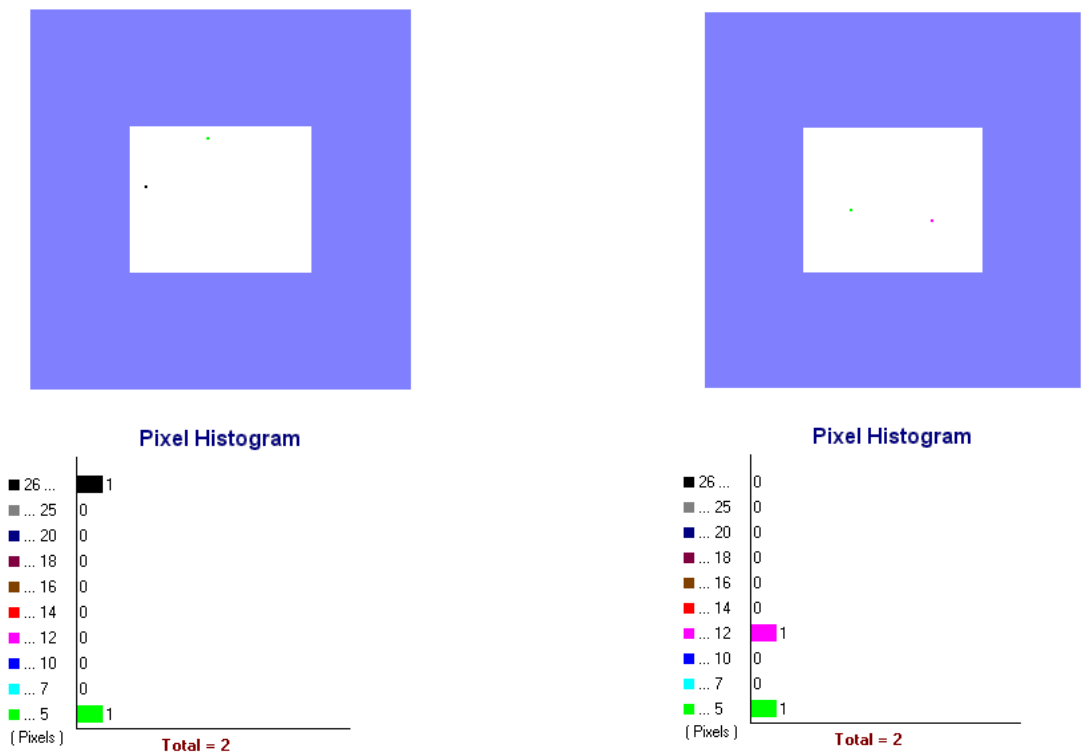

Fig. 2: Particle defect maps of templates cleaned with the POR process, after intentional contamination.

It can be clearly observed from these images that the non-acid POR cleaning process successfully removed cured imprint resist contamination. The POR cleaning technology in this study utilizes photolyzed O_3 water as an alternative to acid cleaning or conventional DI-O_3 cleaning. DI-O_3 photolysis is carried out in a three-step process: (1) light induced homolysis of O_3 in water, (2) the oxygen atom produced reacts with water to form hydrogen peroxide, (3) hydrogen peroxide further phtolyzes to produce hydroxyl radicals [8].

Hydroxyl radicals have higher oxidation potential (2.8V) as compared to ozone (2.07V) and consequently are much more potent oxidizing agents. When such hydroxyl radicals are exposed to cured imprint resist materials or other organic

compounds (C-H) they react primarily by hydrogen abstraction (de-protonation) to produce an organic radical (R`) (4), which reacts quickly with dissolved oxygen to yield an intermediate organic peroxyl (RO2') (5). These intermediates initiate thermal (chain) reactions of oxidative degradation, leading finally to carbon dioxide, water, and inorganic salts [9].

$$O_3 + h\nu \rightarrow O_2 + O('D) \quad (1)$$
$$O('D) + H_2O \rightarrow H_2O_2 \quad (2)$$
$$H_2O_2 + h\nu \rightarrow HO' + HO' \quad (3)$$
$$HO' + RH \rightarrow R' + H_2O \quad (4)$$
$$R' + O_2 \rightarrow RO_2^- \quad (5)$$

The innovative POR cleaning method is faster at removing highly cross-linked imprint resist materials and organic residues from NIL templates. It is a much cleaner, greener alternative to conventional acid processes and as such eliminates the typical costs associated with specialized handling and waste disposal.

3.2 Surface Roughness

Ammonium Hydroxide (NH_4OH) is a known etchant for SiO_2 surfaces and may induce surface roughness if concentration and temperature is not optimized. [10]. Elimination of NH_4OH is not an option as it is essential for inorganic particle removal from the template surface. Two different concentrations (POR and 2.5 times higher than POR) of NH_4OH were used to test surface roughness change induced by cleaning. Figure 3 shows the template surface roughness, rms values before and after 20x cleans with the POR NH_4OH concentration. Roughness was measured at various locations on the template and average values are reported. The roughness change observed was within the AFM error margin. Figure 4 shows rms roughness change before/after cleaning with a >POR (~2.5x) NH_4OH concentration. Although the rms roughness change was higher than POR, it was still in the AFM measurement error range.

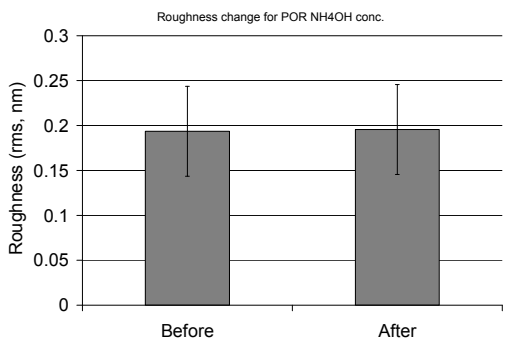

Fig. 3.a: Plot showing roughness values before and after 20x clean with POR NH_4OH concentration

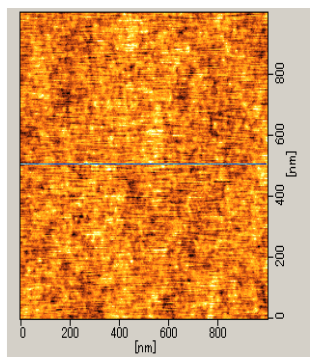

Fig. 3.b: AFM image showing roughness scans before cleaning

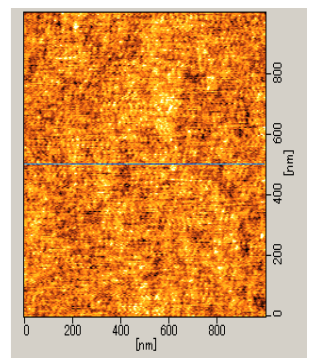

Fig. 3.c: AFM image showing roughness scans after 20x cleaning

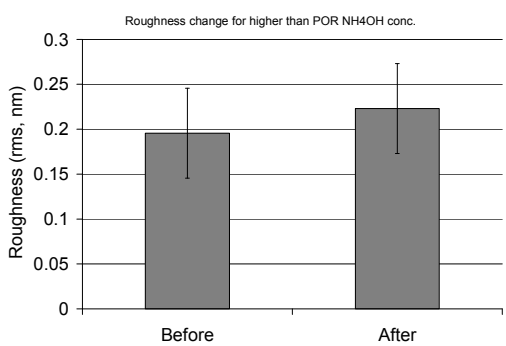

Fig. 4.a: Plot showing roughness values before and after 20x clean with 2.5x POR NH_4OH concentration

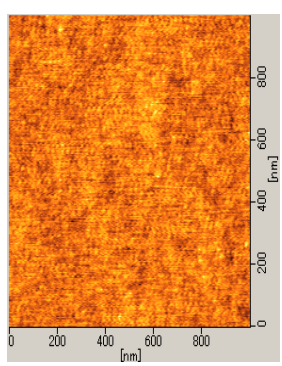

Fig. 4.b: AFM image showing roughness scans before cleaning

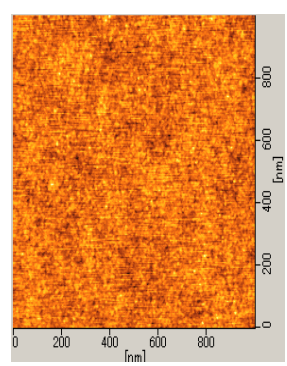

Fig. 4.c: AFM image showing roughness scans after 20x cleaning

3.3 Critical Dimension (CD) Change

NIL template features are etched directly into the quartz resulting in a patterned structure (side-wall, etc.) material that is also quartz. NH_4OH can chemically erode quartz and therefore it is important to determine if there are any cleaning

effects on CD stability. As seen in Figure 5 a template cleaned 20x using the standard POR NH_4OH concentration resulted in only 0.3649nm of CD change or 0.0182nm per clean. This indicates that template can withstand multiple cleaning cycles within its lifetime with little effect on feature size. The > POR NH_4OH concentration resulted in 0.5823nm CD change after 20x cleans or 0.0291nm per clean. The higher ammonia concentration accelerated quartz damage and indicated that the concentration must be optimized.

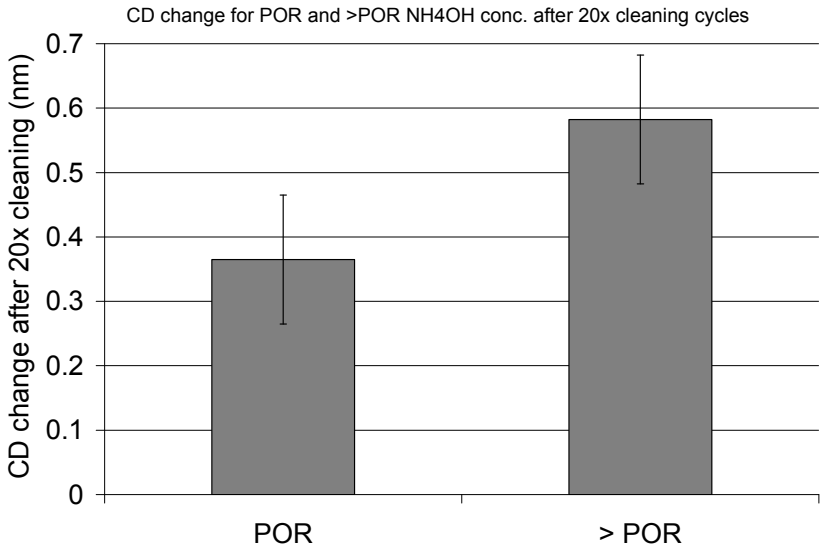

Fig. 5: Plot showing CD change of the quartz features after 20x cleaning cycles with POR ammonia concentration and a 2.5 times higher ammonia, respectively, the higher the concentration the larger the resulting CD change.

3.4 Pattern Damage

To achieve maximum particle removal efficiency, aggressive physical force techniques were used on the templates. The fragile features of the NIL template are prone to physical force damage and a highly controlled process is required. Two of the most commonly used physical force particle removal techniques are MegaSonic and binary spray. In this study both of these methods were applied and the resulting physical force damage was observed. Figure 6 shows the SEM images of the line space pattern before and after POR cleaning. No pattern damage was observed on the 28nm features (aspect ratio 4:1) in any of the 81 locations inspected under SEM.

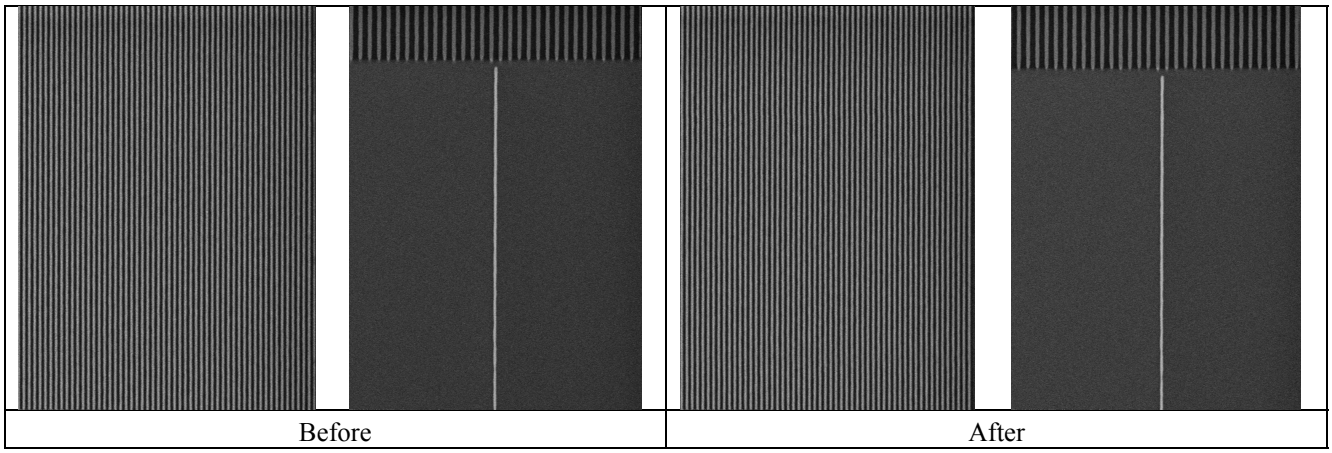

Fig. 6: SEM images showing pattern structure before and after cleaning; not pattern damage is observed.

3.5 Chrome Thickness Loss

Some pattern media templates have a very thin Chrome (Cr) layer as the top surface layer. Chrome is especially sensitive to oxidizing chemistries typically used in conventional mask and wafer cleaning e.g. SPM (H_2SO_4+H_2O_2), Ozone Water

(DI-O3), Plasma ashing, etc. However, these chemistries are also essential for organic removal. Therefore it is important to optimize the cleaning process to effectively remove organics and preserve the Cr layer during template cleaning.
In this study, an innovative non-acid cleaning method based on ozone photolysis was used (explained in section 3.1). The hydroxyl radicals produced from ozone photolysis selectively react with organic materials without significant damage to metal layers. Figure 7 below shows Cr thickness loss after a single cleaning cycle for 3 different samples. The Cr loss was less than 0.5 Angstrom on the average. More data on Cr preservation (using this method for 193i binary photomask) can be found in references 5 & 6.

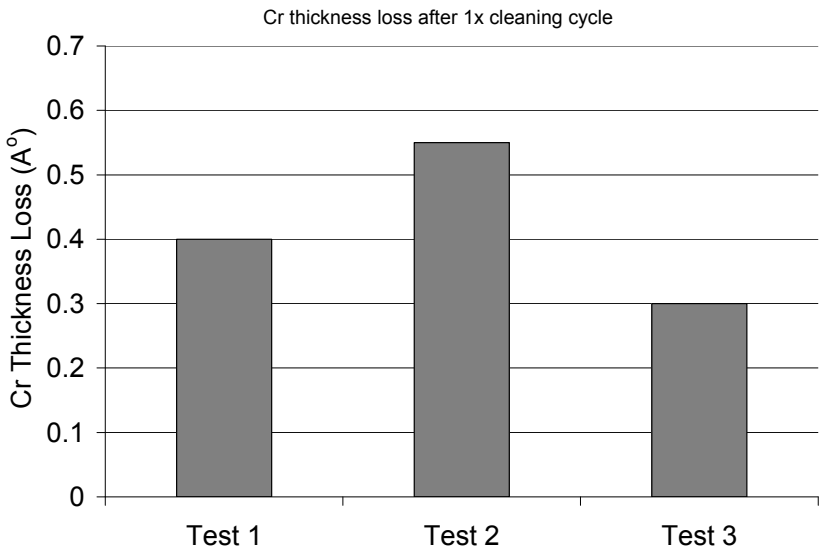

Fig. 7: Plot showing Cr thickness loss per cleaning cycle

3.6 Particle Removal Efficiency

Particle removal efficiency (PRE) was evaluated by depositing SiN and SiO_2 particles on quartz templates. PRE depends on a combination of aggressiveness of physical force (MegaSonic + Binary Spray), duration of physical force (Time), chemistry used and its concentration (zeta potential control, etc.), type of deposited particles (SiN, SiO_2, PSL, etc.) and surface they are deposited on (Cr, MoSi, Quartz, etc.) among other factors. As explained in section 3.4, the aggressiveness of the advanced MegaSonic and Binary Spray was optimized for a pattern damage-free process. PRE was tested under these same conditions and then again after optimization of duration or time of treatment. Figure 8.a shows effect of time on PRE. Reducing the process time to 40% and 20% of the POR time showed 98% and 80% of PRE (normalized) respectively. Increasing the ammonia concentration from POR concentration to 2.5x of the POR concentration only improved PRE by 3% (figure 3.b).

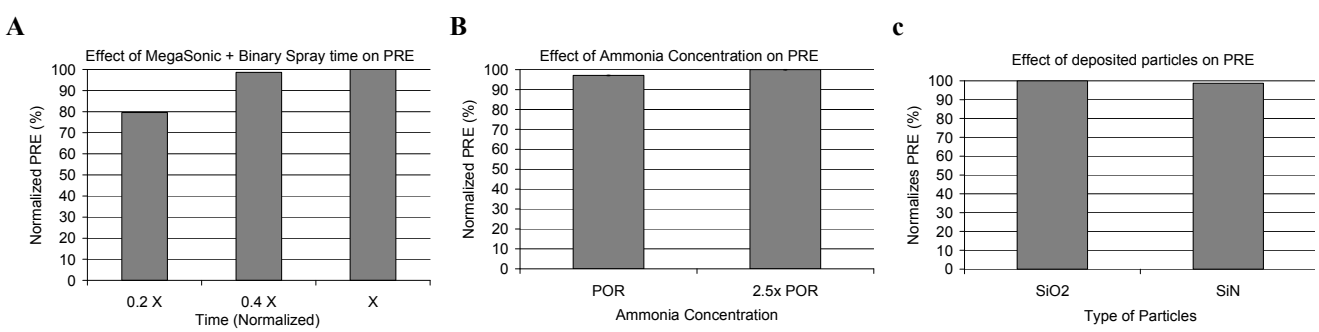

Fig. 8: Plots showing PRE dependence on a) Time b) Ammonia Concentration c) Type of deposited particles.

Different kind of particles can be expected on a template with different adhesion to the underlying surface. Figure 8.c compares the removal of SiN and SiO_2 particles from the template surface. Both particles were removed with almost

equal particle removal efficiencies. These results indicate that the cleaning process can be optimized for any type of particle with equal effectiveness.

3. CONCLUSIONS

The acid-free process successfully removed all residual imprint resist from the 65mm template surfaces. The roughness change before and after 20x cleans was negligible and fell within the AFM error margin. The POR NH_4OH clean induced CD change rates of <0.018nm/clean while higher concentration than the POR increased CD loss but still remained within acceptable limits. A combination of MegaSonic and binary spray process produced no pattern damage on 24nm L/S pattern with a 4:1 aspect ratio. The Cr loss was less than 0.5A^{o}. Process was successfully optimized for maximum particle removal efficiency. A cleaning Process of Record to ensure NIL template integrity was established.

ACKNOWLEDGEMENT

Authors would also like to acknowledge their co-workers at SUSS MicroTec, HamaTech APE and DNP for their help during various stages of this study.

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