Improved adhesion of novolac and epoxy based resists by cationic organic materials on critical substrates for high volume patterning applications

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ABSTRACT

Microlithography uses a variety of resists and polymer materials to create patterns and lithographic structures on several types of substrates. Excellent adhesion of the resists and polymers to the substrate is a prerequisite for successful patterning and pattern transfer. This paper presents the results of an investigation of the effects of an adhesion promoter, SurPass, on the lithographic process when used in combination with a variety of resists, and substrate materials. SurPass is a waterborne, non-hazardous, cationic organic surface active agent that promotes adhesion by modifying the substrate surface energy without deposition, chemical change or impact on electrical properties of the substrate material. The effectiveness of SurPass in combination with several novolac and epoxy resists on various substrate materials will be presented.

Keywords: adhesion, surface promoter, substrates, surface energy

1. INTRODUCTION

Microlithography uses a variety of resists and polymer materials, in combination with a range of substrate materials, as required to obtain the desired properties for the manufactured device.

Examples of substrate materials include silicon, a semiconductor, for use as a carrier substrate for mould fabrication. Semiconducting materials III-V (GaAs, InP, GaP or a combination of them) and ceramic substrates (such as sapphire Al_2O_3, AlN and ZrO_2) are primarily used in microelectronic and optoelectronic applications and for the manufacture of high-power, high frequency electronics such as laser diodes and LEDs. Additionally, substrate materials may be selected for electroplating (TiOx, Au, Cu) properties and for wet/ dry etch fabrication processes (SiO_2, ITO, glass, ceramics, metals, etc.).

Patterning of substrates is performed by exposure of resist and polymer materials by various photon, electron, and ion beam processes. Examples of commonly used resist material for soft mask fabrication include diazonaphthochinone (DNQ)/ phenolic or novolac resins resists (AZ-type resist, ma-P 1200) and aromatic bisazide/ novolac single layer lift-off resists such as ma-N 1400, ma-N 400 [1, 2]. Permanent three dimensional microlithographic structures can also be created using epoxy resist (SU-8) [3] and inorganic hydrogen silsesquioxane (HSQ) resist [4].

Adhesion of the resist material to the substrate is critical for preventing disruptive defects in patterning and pattern transfer such as up-lifting by outgassing and decomposition during resist exposure, delamination and undercutting during resist development. In addition, many microlithographic fabrication processes include additive (electroplating, physical/ chemical vapour deposition) and substractive (wet/ dry etching) multi-step procedures during which previously manufactured features must remain intact. Any adhesion related defects that occur in the patterning and lithographic process are amplified at each process step.

Hexamethyldisilazane (HMDS) is often employed in silicon semiconductor manufacturing as an effective resist adhesion promoter. HMDS is well understood to function on silicon by converting hydrophilic silano groups on the substrate surface to hydrophobic siloxanes. It is believed that the improvement in adhesion is achieved by minimizing the film stress in solvent based hydrophobic resist when coated on hydrophilic substrates. HMDS functionality is limited to silicon based substrates and results vary depending on the type of resist used. HMDS is also prone insufficient or over - priming, is highly sensitive to moisture, and poses health, safety and environmental issues.

In contrast, the SurPass cationic adhesion promoter effectively modifies the surface energy of a broad range of substrate materials for improved surface energy compatibility with a wide range of resist materials without chemically altering the wafer surface. SurPass is unaffected by substrate moisture content, and is waterborne and non-hazardous. SurPass is available in two formulation, SurPass 3000 and SurPass 4000, both of which are examined here. After resist development, substrates prepared with SurPass require no additional processing of lithographic patterns and are ready for subsequent pattern transfer process.

2. EXPERIMENTAL

2.1 Resist materials

Three photo-resist type materials were selected for their applicability and beneficiality to critical substrates used in high volume pattering application. These include two novolac resin resists and a chemically amplified epoxy resist.

Positive tone novolac resist: ma-P 1200 DNQ/ novolac based resist series as representative of positive resist for conventional patterning processes used in wet and dry chemical etching as well as for electroplating processes.

Negative tone novolac resist: ma-N 400 and ma-N 1400 aromatic bisazide/ novolac based resist series developed for pattern transfer process via physical vapor deposition (PVD), such as evaporation of metals and sputtering and lift-off processes.

Negative tone epoxy resist: SU-8 is a chemically amplified epoxy resist that uses a photo acid generator dissolved in a solvent, either γ butyrolactone (SU-8 series) or cyclopentanone (SU-8 2000 series). This famous representative of negative tone epoxy resists is used to form highly cross-linked structures in the manufacture of permanent and non-permanent patterns for micro fluidics, micro optics, and MEMS applications.

2.2 Substrate materials

Novolac resist application: Positive and negative tone novolac resists were processed using substrate materials representative of semiconductor manufacturing and in wet etch and PVD applications, as well as for electroplating. These include silicon, glass, SiO_2, copper as seed layer for electroplating, and III-V semiconductor materials such as GaP.

Epoxy resist: SU-8 was patterned on silicon, glass and SiO_2 substrates for applicability for micro fluidic and optoelectronic device fabrication or for PMDS mould manufacturing; on gold coated silicon or on TiOx used as a seed layer for subsequent electroplating processes.

2.3 Sample preparation: substrate pre-treatment and adhesion promoter

Substrate cleaning: New substrate samples were prepared for resist coating without any additional cleaning step. As pre-treatment additionally a short oxygen plasma cleaning step, and a dehydration bake (DHB) at 180 °C for at least 10 min on a hotplate is applied for the removal of any kind of humidity.

The substrates were further prepared with either no pretreatment for improved adhesion (control), HMDS pretreatment by liquid or vapor application (Si containing substrates only) or with SurPass adhesion promoter for evaluation of resist adhesion, improved pattern resolution, and resist performance.

The substrates were treated with SurPass adhesion promoter for evaluation of improved pattern resolution and resist performance. SurPass is characterized as a waterborne cationic organic surface active agent that functions by modifying the surface energy of the substrate and optimizing zeta potential for greatly improved resist adhesion and performance [5]. Previous studies of SurPass treated substrates show no deposition, chemical, or other physical changes to the substrates when examined by x-ray photoelectron spectroscopy (XPS) [6]. In addition, SurPass does not generate volatile organic compounds (VOC) or break down products, such as ammonia, during application, and may eliminate the need for a dehydration back prior to resist coating. SurPass is manufactured in two versions designated as SurPass 3000 and

SurPass 4000. SurPass 3000 is mildly acidic and contains a cleaning surfactant for enhanced performance. SurPass 4000 is slightly alkaline and contains no additives. Suitability of each version was evaluated for specific resist - substrate combinations used by industry. SurPass may applied to the clean substrate by means of dispense (spin coating), spray or immersion, followed by a water or isopropanol (IPA) rinse and nitrogen blow or spin dry. For purposes of is investigation SurPass adhesion promoters were applied by spin coating the solution at 3000 rpm for 30 s, followed by an IPA rinse and nitrogen blow dry.

For comparison, a control group without adhesion promoter treatment was prepared.

Resists were lithographically investigated and samples were prepared according to the guidelines available for each resist series typically on 4 inch substrates. Novolac ma-P 1200 and ma-N 400 and ma-N 1400 resists were spin coated and UV patterned with a thickness ranging from 1.0 to 8 µm. Epoxy SU-8 was spincoated, baked and UV patterned to obtain a layer of about 80 µm. For the UV patterning a UV broadband mask aligner MA 6 (SUSS) was used. Baking was done on hotplates. Development was done by immersion using the recommended/ suitable specific resist developers. Developed resist patterns were nitrogen blow dried. Electroplating of nickel was done using a nickel sulphamate bath at following conditions: pH value: 3-4, temperature: 55 °C, current density: 2A/ dm^2.

2.4 Characterization and evaluation of patterned resist

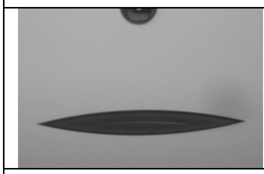
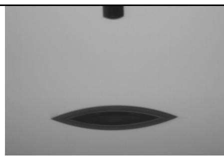
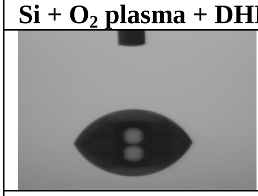
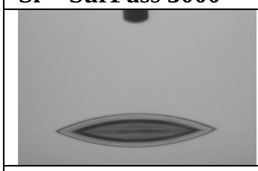
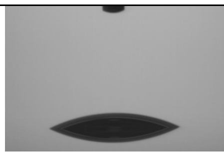
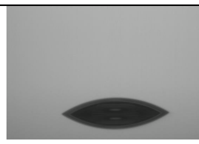
The surface tension or energy of the untreated and pre-treated substrates was characterized by determination of the static contact angle. The static contact angle of a water drop deposited on the substrate indicates the wettability and the hydrophobicity or hydrophilicity of a substrate surface.

The coated and patterned resist layers were inspected visually, by optical microscope and Scanning electron microscopy (SEM). Resist adhesion as well as the initiation and the quality of the electroplating process of nickel patterns were evaluated by SEM of the electroplated patterns.

3. RESULTS AND DISCUSSION

3.1 Surface energy of the untreated and pre-treated silicon substrate

The surface tension or energy of a substrate surface can be tuned by applying a surface pre-treatment and is demonstrated for a silicon (Si) substrate in figure 1.

Si	**Si + O_2 plasma**	**Si + O_2 plasma + dehydration bake (DHB)**
 Θ ~ 14 °	 Θ ~ 20 °	 Θ ~ 10 °
Si + O_2 plasma + DHB + HMDS		
 Θ ~ 65 °		
Si + SurPass 3000	**Si + SurPass 3000 + water rinse**	**Si + SurPass 3000 +IPA rinse**
 Θ ~ 25 °	 Θ ~ 25 °	 Θ ~ 32 °
Si + SurPass 4000	**Si + SurPass 4000 +water rinse**	**Si + SurPass 4000 +IPA rinse**

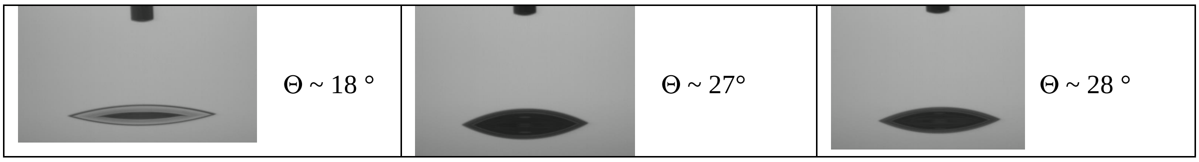


Figure1: Static contact angle (Θ) of a water drop deposited on the untreated or pre-treated silicon (Si) substrate surface, DHB…dehydration bake

The contact angle can be between 0° (high wettability) ≤ Θ ≥ 180° (no wettability). When an oxygen plasma is applied to form silicon dioxide the surface becomes hydrophilic (Θ ~ 20°). The DHB leads to an even more hydrophilic surface (Θ ~ 10°). The application of HMDS reduces the wettability with water and the surface becomes less hydrophilic (Θ ~ 65°). The application of the SurPass adhesion promoters leads to a less hydrophilic surface (Θ ~ 25°), independent of whether no additional rinse step, a water or an IPA rinse is applied after the SurPass coating. This concludes that the application of an IPA rinse instead of the water rinse leads to same surface energy ready for a subsequent resist application.

3.2 Results of the adhesion improvement of positive tone ma-P 1200 DNQ/ novolac resist series

For the initial evaluation of SurPass adhesion promotion both primer versions – SurPass 3000 and SurPass 4000 - were investigated on silicon substrates. In subsequent experiments on several other substrates only SurPass 4000 was applied and investigated (Fig.2).

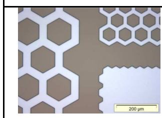
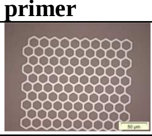
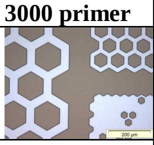
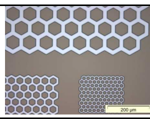
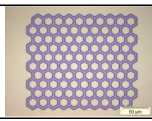
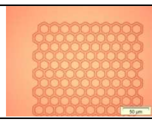
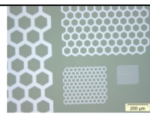
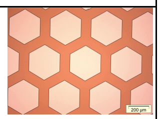
ma-P 1200, Film thickness = 7.5 µm, development in 0.22 to 0.26 N TMAH							
Si substrate				**SiO_2 substrate**	**Glass substrate**	**GaP substrate**	**Cu surface**
Control	**HMDS primer**	**SurPass 3000 primer**	**SurPass 4000 primer**				
							
Bad adhesion for smaller patterns	Excellent adhesion	Reduced adhesion	Excellent adhesion	Excellent adhesion	Excellent adhesion	Excellent adhesion	Excellent adhesion

Figure 2: Optical microscope of ma-P 1200 DNQ/ novolak patterns on several substrates with and without application of SurPass adhesion promoters

Good adhesion was observed when SurPass 4000 as adhesion promoter is applied in combination with the positive tone ma-P 1200 DNQ/ novolak based resist on investigated substrate materials, even when the critical substrate copper is used. A thin copper layer deposited on a silicon carrier wafer used as seed layer for a subsequent electroplating process and is highly critical since it reacts very fast with humidity to form copper hydroxide, that can cause bad adhesion, residues after the development process or less adhesion of metallic electroplated patterns.

A tendency to obtain a higher resolution of novolac resist when SurPass adhesion promoter is applied was observed and previously shown for electron beam exposure of HSQ resist on InGaAs substrates [6].

3.3 Results of the adhesion improvement of negative tone ma-N 400 and ma-N 1400 aromatic bisazide/ novolac based resist series

For the initial evaluation of SurPass adhesion promotion both primers versions – SurPass 3000 and SurPass 4000 - were investigated on silicon substrates. In subsequent experiments on several other substrates only SurPass 4000 was applied and investigated (Fig.3, 4).

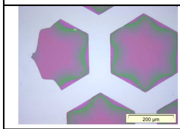
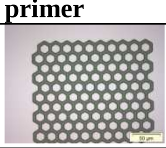
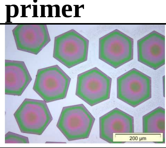
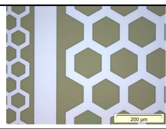
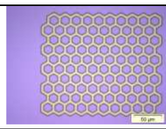
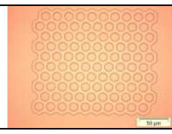
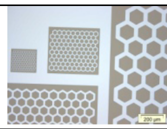
ma-N 1400, Film thickness: = 1.0 µm, development in ma-D 533/S or 0.363 N TMAH						
Silicon substrate				**SiO_2 substrate**	**Glass substrate**	**GaP substrate**
Control	**HMDS primer**	**SurPass 3000 primer**	**SurPass 4000 primer**			
						
Bad adhesion	Excellent adhesion	Bad adhesion	Excellent adhesion	Excellent adhesion	Excellent adhesion	Excellent adhesion

Figure 3: Optical microscope of ma-N 1400 aromatic bisazide/ novolak patterns on several substrates with and without application of SurPass adhesion promoters

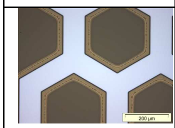
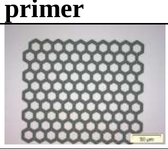
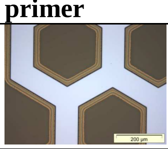
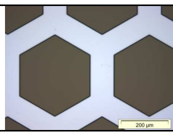
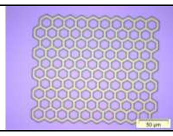
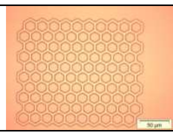
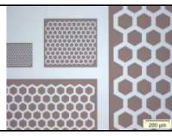
ma-N 400, Film thickness = 7.5 µm, development in ma-D 332/S or 0.2 N NaOH or 0.275 N TMAH						
Silicon substrate				**SiO_2 substrate**	**Glass substrate**	**GaP substrate**
Control	**HMDS primer**	**SurPass 3000 primer**	**SurPass 4000 primer**			
						
Bad adhesion	Excellent adhesion	Bad adhesion, residues on the developed areas	Excellent adhesion	Excellent adhesion	Excellent adhesion	Excellent adhesion

Figure 4: Optical microscope of ma-N 400 aromatic bisazide/ novolak resist on several substrates with and without application of SurPass adhesion promoters

Good adhesion was observed when SurPass 4000 was applied as an adhesion promoter in combination with the negative tone novolak based resists. A tendency to obtain a higher resolution when SurPass adhesion promoter is applied was also observed.

3.4 Results of the adhesion improvement of negative tone SU-8 epoxy resist

For the initial evaluation of SurPass adhesion promotion both primer versions – SurPass 3000 and SurPass 4000 were investigated/ applied on silicon substrates (Fig.5).

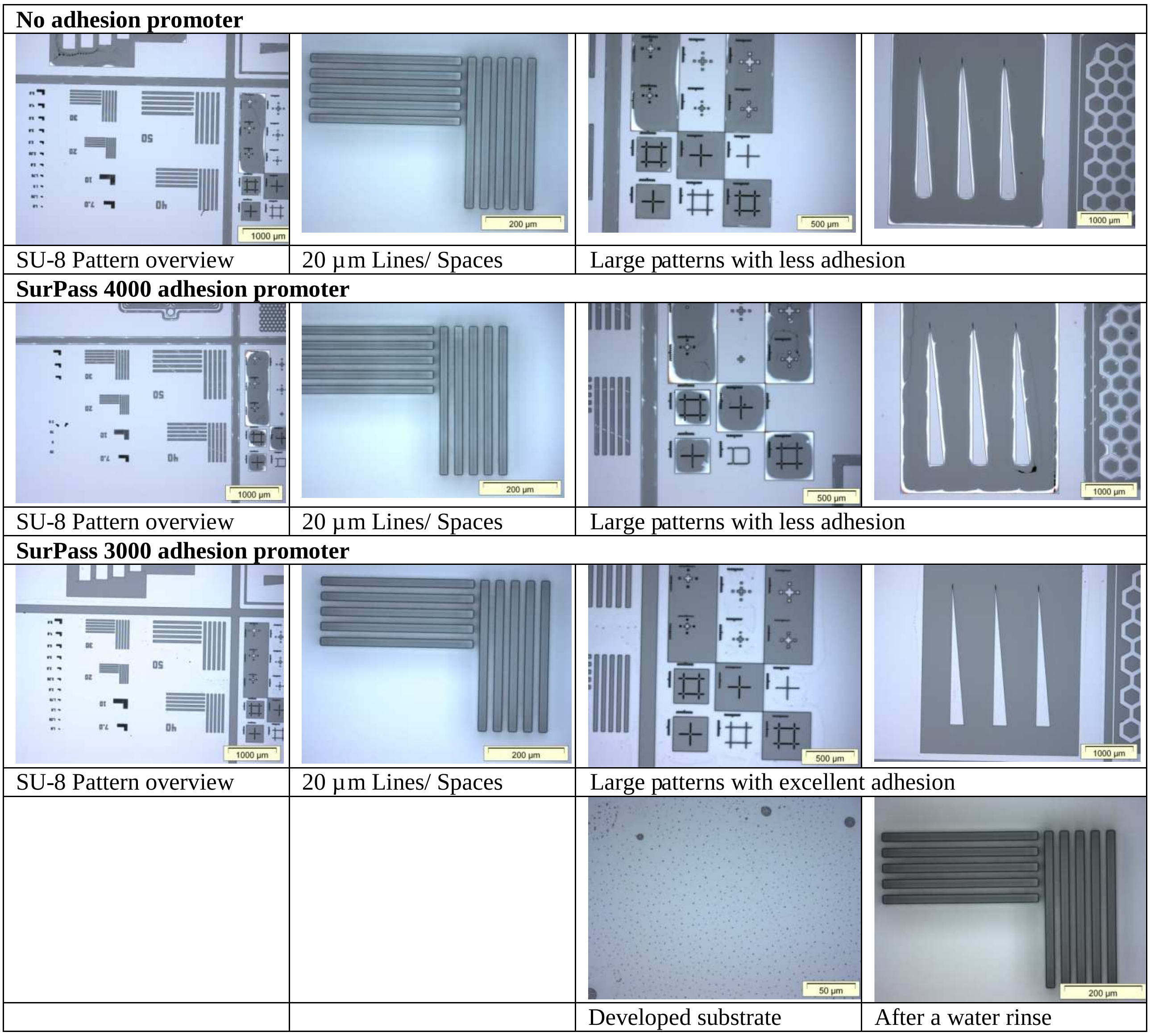


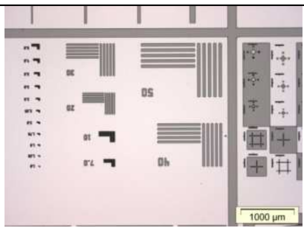
Figure 5: Optical microscope pictures of UV patterned SU-8 (80 µm thick) on silicon substrates without and with application of SurPass adhesion promoter

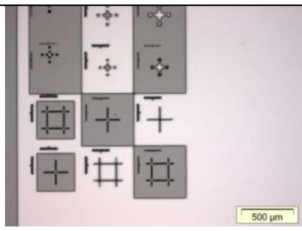
Good adhesion for SU-8 resist patterns was obtained using SurPass 3000 as an adhesion promoter.

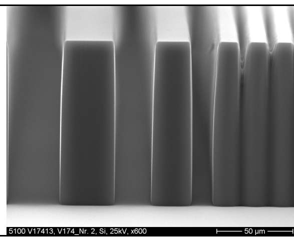
Development of the exposed SU-8 patterns was done as recommended in propylene glycol monomethyl ether acetate (PGMEA), followed by an IPA rinse. After the IPA rinse droplet like residues were observed in the developed areas. Since the application of a water rinse is recommended, a water rinse followed by an additional IPA rinse of the developed patterns was done. It seems that a water rinse is required when SurPass 3000 adhesion promoter is applied since these kinds of droplet like residues are removable by applying a water rinse step after the solvent based development. An IPA rinse after the water rinse step of the developed patterns improves the drying of the developed and rinsed patterns.

In subsequent experiments concerning adhesion improvement of SU-8 resist patterns on substrates other silicon only SurPass 3000 was applied and is shown figure 6.

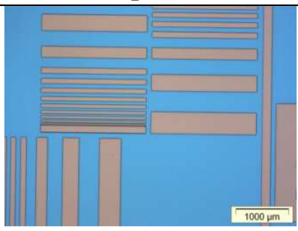
Substrate: Si ⇒ excellent adhesion

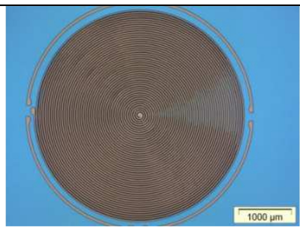


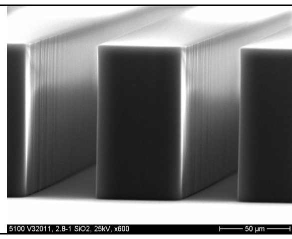




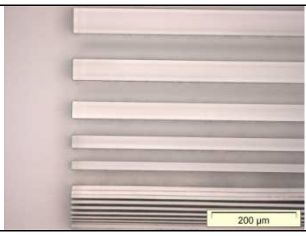
Substrate: SiO_2 ⇒ excellent adhesion

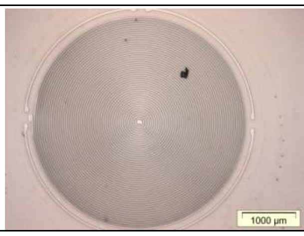


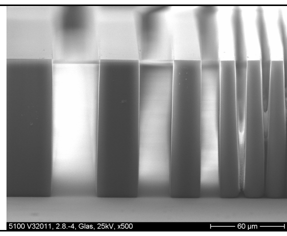




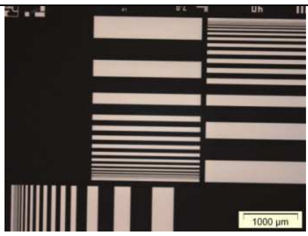
Substrate: Glass ⇒ excellent adhesion

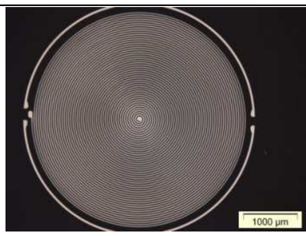


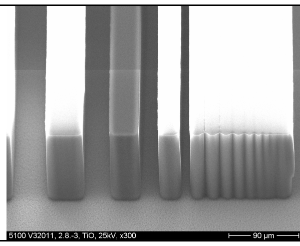




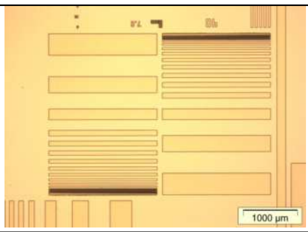
Substrate: TiOx ⇒ excellent adhesion

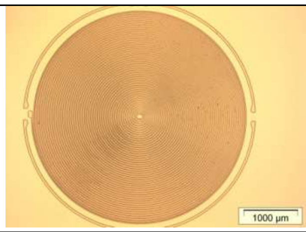






Substrate: Cr/ Gold on silicon ⇒ excellent adhesion





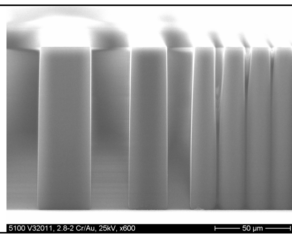


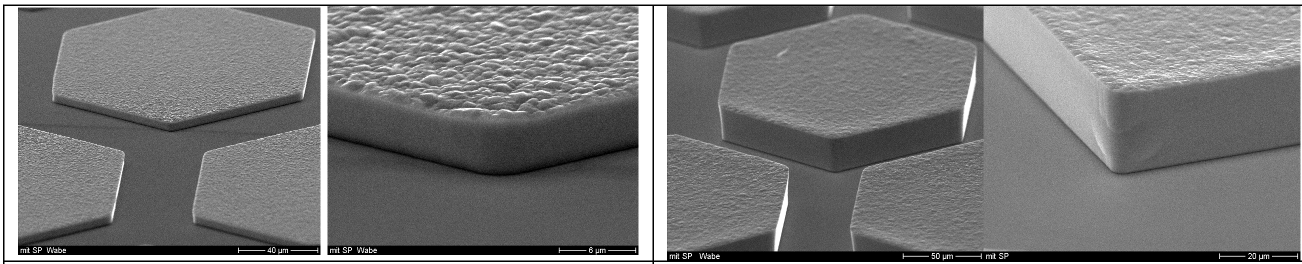
Figure 6: Optical microscope and SEM pictures of SU-8 resist on several substrates after application of SurPass 3000 adhesion promoter, resist on all substrates was lithographically processed with an identical parameter set (without any optimization regarding the used substrate)

The application of SurPass 3000 adhesion promoter improves the SU-8 adhesion on all investigated substrates. An additional water rinse step followed by an IPA rinse step after the solvent based development is recommended and prepares the resist patterns for the subsequent pattern transfer process.

3.5 Electroplating of nickel in a ma-P 1200 resist mould on copper substrate

Metallic nickel was electroplated on a ma-P 1200 resist mould on copper as thin seed layer on a silicon carrier substrate to determine the cleanness of the substrate after application of SurPass 4000 adhesion promoter as well as the adhesion of the resist mould and of the electroplated patterns. The positive resist was patterned according the standard recipe and after development the dried ma-P 1200 mould patterns were used for the electroplating process without any additional treatment step. Results are shown in figure 7.

Nickel patterns were successfully electroplated without any defect.



Thickness ma-P 1200 resist mould: 7.5 µm Thickness electroplated Ni patterns: 5 µm	Thickness ma-P 1200 resist mould: 30 µm Thickness electroplated Ni patterns: 25 µm

Figure 7: SEM pictures of electroplated nickel patterns

4. CONCLUSIONS

The improvement of the resist adhesion on several substrates for novolac and epoxy resin based resist series was demonstrated. Depending on the nature of the resists either SurPass 3000 or SurPass 4000 is recommended to use. SurPass 3000 is recommended for use in combination with an epoxy based resist, such as SU-8 with excellent results and for the SU-8 mould preparation on metallic substrates, such as gold substrates. A water rinse step has to be applied as additional process step after the development to remove droplet like residues and to prepare the substrate surface for subsequent pattern transfer processes. SurPass 4000 is recommended to use in combination with novolac based resists and works perfectly on silicon or typical III-V semiconductor substrates. SurPass 4000 is suited to be applied for DNQ/ novolac as well as for aromatic bisazide/ novolac resist series. Since it was already demonstrated that SurPass also works perfectly with HSQ resist [6] it is assumed that SurPass adhesion promoter can also be applied for improved performance with other available resists with different resist chemistry and compositions as the investigated materials.

Subsequent nickel electroplating in a patterned ma-P 1200 DNQ/ novolac resist mould on copper as seed layer showed excellent resist as well nickel adhesion on to the substrate. Nickel patterns were successfully electroplated without any defect.

REFERENCES

[1] Toepper, M., Voigt, A., Heinrich, M., Hauck, K., Mientus, R., Gruetzner, G., Ehrmann, O. „A single layer negative tone lift-off photo resist for patterning a magnetron sputtered Ti/Pt/Au contact system and for solder bumps" Microelectronic engineering 78/79 (2005) 503-508

[2] Moser, D., Heinrich, M., Schuster, Ch., Klukowska, A., Schmidt, A. „Entwicklung und Charakterisierung eines Prozesses zur Herstellung von Mikrolinsen mittels Lithographie, RIE und UV-Abformung" MikroSystemTechnik - KONGRESS 2009 12.10.2009 - 14.10.2009 Berlin

[3] Lorenz, L., Despont, M., Vettiger, P., Renaud, P. „Fabrication of photoplastic high aspect ratio microparts and micromolds using SU-8 UV resist" Microsystems Technology 4 (1998) 143 - 146

[4] Grigorescu, A. E., Hagen, C. W. "Resists for sub-20 nm electron beam lithography with a focus on HSQ: state of the art" Nanotechnology 20 (2009) 292001 (31pp)

[5] Hodgson, L., Thompson, A. "Reduced zeta potential through use a cationic adhesion promoter for improved resist performance and minimizing material consumption." Proc. SPIE Vol. 8325 Advances in Resist Materials and Processing Technologies XXIX 83251W-1 (2012)

[6] Erfurth, W., Thompson, A., Ünal, N. "Electron dose reduction through improved adhesion by cationic organic material with HSQ resist on an InGaAs multilayer system on GaAs substrate" *Proc. SPIE* 8682, Advances in Resist Materials and Processing Technology XXX, 86821Z (March 29, 2013)