Fabrication of Three-Dimensional Imprint Lithography Templates by Colloidal Dispersions

A. Marcia Almanza-Workman, Taussig P. Carl, Albert H. Jeans, Robert L. Cobene

HP Laboratories
HPL-2011-32

Abstract:

Self-aligned imprint lithography (SAIL) enables patterning and alignment of submicron-sized features on flexible substrates in the roll-to roll (R2R) environment. Soft molds made of elastomers have been used as stamps to pattern three-dimensional masks. Durability of these stamps is one factor that limits their efficiency in a R2R process. Fluorothermoplastics are low cost imprint stamp materials with great mechanical strength and chemical compatibility but with low gas permeability that trap air bubbles in the photopolymer during the imprint process. This paper describes the strategy for increasing gas permeability of fluorothermoplastics by introducing voids in the stamp by using aqueous colloidal dispersions of fluorothermoplastic nanoparticles. The hard fluorinated particles, whose modulus is too high to deform during drying, remain as hard spheres and lead to a porous packing when drying is complete. The selection of additives to eliminate cracks created during water evaporation is also described in this paper.

Fabrication of Three-Dimensional Imprint Lithography Templates by Colloidal Dispersions

A. Marcia Almanza-Workman,**[a]* **Carl P. Taussig,**[b] **Albert H. Jeans,**[b] **Robert L. Cobene**[b]

5

Self-aligned imprint lithography (SAIL) enables the patterning and alignment of submicron-sized features on meter-scaled flexible substrates in the roll-to roll (R2R) environment. SAIL solves the problem of precision interlayer registry on a moving web by encoding all the geometry information required for the entire patterning steps into a monolithic three-dimensional mask that is imprinted on the thin film stack
10 deposited on a flexible substrate. Soft molds made of plastics or elastomers cast on a silicon master have been used as stamps to pattern the 3D masks because of their low cost and ease of fabrication. However, the durability of these stamps is one factor that limits their efficiency in a R2R process. Fluorothermoplastics are low cost imprint stamp materials with great mechanical strength and chemical compatibility but with low gas permeability that trap air bubbles in the photopolymer during the imprint
15 process. This paper describes the strategy for increasing gas permeability of fluorothermoplastics by introducing voids or pores in the stamp material by fabricating the stamps with aqueous colloidal dispersions of tetrafluoroethylene-hexafluoropropylene copolymer (FEP) nanoparticles. The basic idea is that the hard fluorinated particles, whose modulus is too high to deform during drying, remain as hard spheres and lead to a porous packing when drying is complete. The selection of suitable additives to
20 eliminate cracks created by capillary stresses during water evaporation is also described in this paper.

Introduction

Significant interest has arisen in low cost flexible electronics for display applications, electronic wallpaper, signage, clothing based displays, and wearable electronics. Flexible substrates
25 undergo non-uniform deformations during device fabrication so the usual photolithographic tools requiring precise layer-to-layer alignment are difficult and costly to implement. The problem of layer-to-layer alignment has been solved using a self-aligned imprint lithographic process (SAIL)[1-3] by encoding all the
30 geometry information required for the entire patterning steps into a monolithic three-dimensional mask that is imprinted on the thin film stack deposited on a flexible substrate (Fig. 1). Since this monolithic masking structure distorts with the substrate, alignments are preserved throughout subsequent processing. The
35 SAIL process enables the patterning and alignment of submicron-sized features on meter-scaled flexible substrates in a roll-to-roll (R2R) environment. Using a sequence of etch steps to alternately etch the substrate and thin the mask, an array of thin film transistors that serves as an active matrix backplane for a flexible
40 display can be fabricated. Since all the masking layers are created simultaneously, their relative alignment is maintained even if the substrate undergoes large distortions.

The 3D masters for the imprint process are made using conventional photolithography. This gives good control of critical
45 dimensions and other geometrical attributes such as side wall draft angle to facilitate release of molded structures. Typical step heights are about 0.7 to 1.0 microns. Larger step heights provide

more margin in the subsequent etching steps but require longer etching times and can result in loss of critical dimensions. Silicon
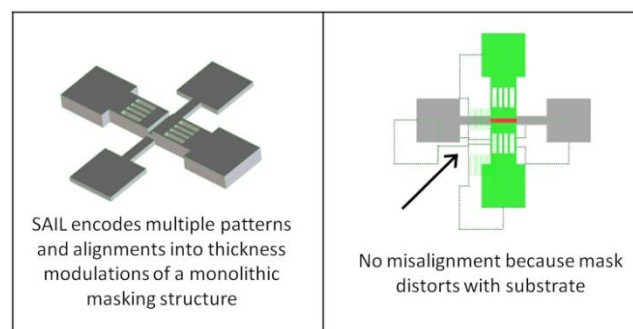50 master fabrication of the 3D patterning is described elsewhere.[4]

Fig. 1 Unique feature of the SAIL process to preserve interlayer alignments

Soft molds made of plastics or elastomers cast on a master
55 have been used because of their low cost and ease of fabrication. However, the durability of these coatings is one factor that limits their efficiency in a R2R process. A typical run length for a R2R process is 1-2 km. This requires that the elastomeric imprinting stamp must provide at least 1000 impressions without
60 degradation (assuming a 1 m circumference of the imprinting roller). The optimum stamp material should satisfy all the requirements listed in Table 1.

Table 1 Stamp requirements for SAIL roll-to-roll processes

CHEMICAL	SURFACE CHEMISTRY	MECHANICAL
• UV transparent	• Good release from master	• Low thermal expansion
• High resolution and fidelity	• Good release from photopolymer	• Flexible
• Low and reproducible shrinkage	• Compatible with adhesives used to adhere stamp to quartz roller	• Excellent compression set
• Low swelling with changes in %RH		• Compliant
• Without unsaturated groups that can react with acrylated/methacrylated photopolymers		• High softening temperature
• High gas permeability		• High fracture toughness
• Chemically inert		• Excellent replication
		• Abrasion resistance

To date a large number of soft and flexible molds have been used in imprinting techniques. Examples of materials used to make soft molds include poly(dimethylsiloxane) PDMS,[1,5-7] ester type UV-curable prepolymers,[8] fluorinated organic-inorganic hybrid sol gel resins,[9,10] photo curable perfluoropolyethers (PFPE),[11-13] fluorothermoplastics,[14,15] amorphous fluoropolymer Teflon® AF,[16,17] and fluoro-silsesquioxanes.[18,19]

Polydimethylsiloxane (PDMS) is the most commonly used material as an imprint lithography stamp but it is poorly suited for a high volume R2R process due to mechanical breakage, distortion from swelling, adhesion of the photopolymer to the stamp and its inability to produce closely spaced submicron features due to pairing. In addition, the shrinkage and deformation of PDMS during thermal curing can result in loss of critical dimensions.

Teflon® AF (amorphous fluoropolymer by Dupont) can have a life greater than 1000 impressions in a very clean environment but is very expensive and too friable leading to damage by particles on the substrate.

PFPE (meth)acrylate based systems suffer from high cost, swelling, and oxygen inhibition during stamp fabrication leading to prolonged UV curing in an inert environment.
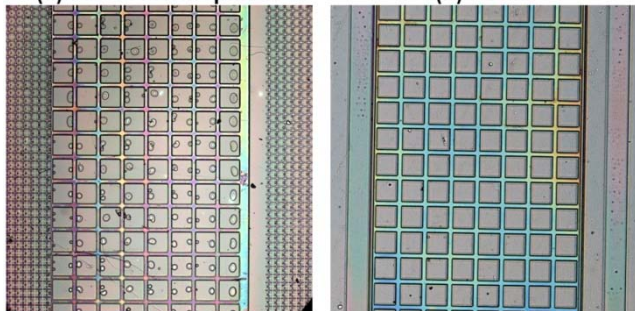

Fig. 2 Polymer imprinted with (a) low permeability stamp material (fluorothermoplastic), showing regularly occurring air bubbles and (b) high permeability stamp material (PDMS), without trapped bubbles

Fluorinated thermoplastics are attractive as a mold material due to their very low surface energy, solvent resistance, chemical stability, UV transparency, and high modulus. However, they have low gas permeability and air bubbles can be trapped in the photopolymer during imprinting (Fig. 2).[1] A strategy to increase gas permeability is to introduce voids or pores in the stamp material. These voids can be created by coating the master with an aqueous colloidal dispersion of fluorothermoplastic nanoparticles. The basic idea is that the hard fluorinated particles, whose modulus is too high to deform during drying, remain as hard spheres and lead to a porous packing when drying is complete. Unfortunately, cracks can be created by capillary stresses during water evaporation. In this paper, we report the fabrication of imprint stamps by colloidal dispersions of a fluorothermoplastic with suitable additives that eliminate cracking during drying and enhance mechanical strength.

Experimental

Materials

Tetrafluoroethylene-hexafluoropropylene copolymer (FEP) is the preferred non-stick fluorothermoplastic due to its high UV transmission, outstanding chemical resistance and great mechanical strength. FEP is commercially available as a water-based latex dispersion with a particle size of 150 nm and pH of 9.5 under the trade name Dyneon™ FEP 6300G Z (3M Company). Either 150 microns thick FEP film (Norton® FEP Type FG from Saint-Gobain) or 100 microns thick Tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride under the trade name Dyneon™ THV (Ajedium Films, a division of Solvay-Solexis, Inc.) was used as a backing sheet to support and level the latex films during sintering.

Three acrylic latex emulsions (UCAR™ 627, UCAR™ 435 and NEOCAR™ 820, Dow Chemical Co., Midland, MI), with Tg below 20°C and similar pH and particle size to Dyneon™ FEP 6300G Z were considered as deformable particles in this study. Their respective properties are listed in Table 2.

Table 2 Material parameters reported by suppliers

Product	Particle size [microns]	% solids	pH	Tg [°C]	Viscosity [cP]	Acid number
Dyneon™ FEP 6300G Z	0.15	55	9.5	80	65	----
UCAR™ 627	0.11	43	9.5	15	550	7
UCAR™ 435	0.25	45	8.5	19	65	19
NEOCAR™ 820	0.07	45	8.5	20	150	10
Dow HS3020	1	25	7.5-8.5	105	250	----
Dow 23-4426	1	13.5	7.5-8.5	100	----	----

Hollow spherical particles with a porous shell having an average particle size of 1 micron with a carboxylated styrene-acrylate backbone (Dow Chemical Company) under the trade name 23-4426 and HS3020 were evaluated to give additional porosity to the stamp.

Tetraethylene glycol dimethyl ether (TetraGlyme), 1,3-dimethyl-2-imidazolidinone (13DM2I) and butyl carbitol (Carbitol) purchased from Aldrich were used as coalescing solvents.

Carbodilite SV-02 (from Nisshinbo), a waterborne non-ionic polycarbodiimide resin that reacts with carboxyl groups, served as a crosslinking agent of the carboxylic groups in the acrylic latex resins.

4M, a proprietary acrylate-based negative tone imprint etch masking material containing resins and monomers from Sartomer Company Inc., was used as the imprint material. This photopolymer is sensitive to UV light with peak sensitivity around 360-380 nm and is optimized for fast roll-to-roll coating, curing and imprinting with great acid chemical resistance and dry etch resistance.

Characterization methods

Particle size and size distribution of the Dyneon™ FEP dispersion were determined by dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments). The Dispersion Technology Software v5.10 was used to determine mean particle size. The samples were prepared by diluting two drops of the colloidal dispersion in deionized water. The temperature of the cell was kept at approximately 25°C. Each measurement was repeated using four different samples.

Melting temperature (Tm) of the fluoropolymers was measured by differential scanning calorimetry (DSC). The measurement was performed on a TA Instruments model Q100 cooled by liquid nitrogen and under a nitrogen environment. The test sample was equilibrated at –50°C for 5 min followed by heating at a rate of 10°C/min to 350°C. The Universal Analysis 2000 V4.5A software was used to determine Tm. Sheet samples were cut with a 1/4" hole punch. Colloidal dispersions were dried in an argon environment with a thermogravimetric analyzer (TGA Q500 from TA instruments) in DSC aluminium pans. Sufficient wet dispersion was added to the pans to yield 10-15 mg of dried polymer. The pans were capped prior to running the DSC.

The *morphological* observation of the quality of coating, stamp and imprint polymers was performed by scanning electron microscopy (SEM, Philips XL-30 FEG). The samples were gold coated for SEM observation.

UV transmission through the stamps was evaluated with a UV Power Puck II radiometer (EIT, Inc) in the ranges of UVA (320-390nm), UVB (280-320nm), UVC (250-260nm) and UVV (395-445nm). The percent transmission through the stamp was determined by comparing the measured light intensity of a Dymax 5000-EC lamp with type D bulb using a radiometer covered and uncovered with a layer of stamp material.

Preparation of latex dispersions

Monodisperse Dyneon™ FEP dispersion was used as received. Latex blend dispersions were prepared by combining Dyneon™ FEP dispersion with acrylic latex and additives. The latex blend was ultrasonicated for 10 min and filtered with 10 micron Pall Acro 25 Last Chance Syringe filters (LCF-12100) prior to coating preparation.

Preparation of latex stamps

Latex films were prepared by spin coating at 1000 rpm for 60 sec directly onto the 150 mm patterned silicon masters. The coating was then baked at 70°C for 5 min on a hot plate to remove water, followed by higher temperature post-baking (150°C for Carbitol or 13DM2I and 180°C for TetraGlyme) for 10 min to remove the coalescing solvent. The dry thickness of the latex coating was between 3 and 5 microns.
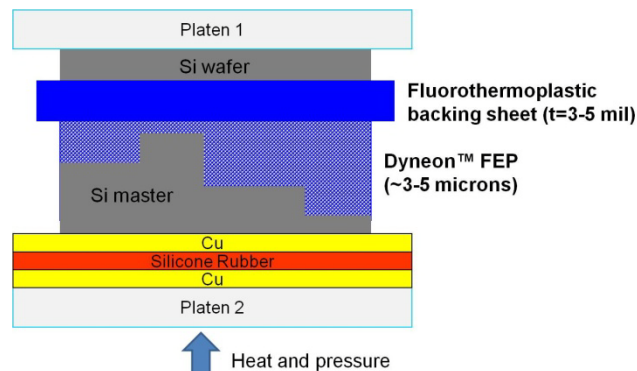

Fig. 3 Embossing and sintering assembly and process

A THV or FEP sheet (pre-cleaned with acetone) was placed between the latex coated master and an unpatterned polished silicon wafer. The particles were sintered to themselves and to the THV or FEP sheet with a manual bench top hydraulic Carver hot press (Model 3851 from Carver Inc., Wabash, IN) equipped with 6" x 6" heating/cooling platens and digital temperature controls. In order to ensure uniform force and thermal distribution on the wafer stack during compression, a red silicone rubber sheet with 70 Shore A hardness (Small Parts, Inc, part no SRR70-0031-E) was sandwiched in between two copper plates and used as a support on the bottom platen. The wafers were placed in the press and pressure was applied at a rate of about one stroke every 2 sec until the desired load was reached. The sample was heated at a rate of 10°C/min from room temperature to the desired temperature, allowed to equilibrate for 5 min, cooled at a rate of 5°C/min by flowing compressed air through the platens, and released from pressure at <30°C. The assembly in the press is shown in Fig. 3.

Hand or roll-to-roll imprinting was used to test chemical compatibility and release of the stamp with 4M imprint photopolymer. Hand imprinting was carried out by slowly applying the latex stamp using a rubber roller against a ~2 micron spin coated photopolymer layer on a silicon wafer. The rubber roller was run a couple of times on the sample to ensure uniform liquid flow, conformation to the features on the stamp and minimize trapped bubbles. The sample was then exposed to UV light (Dymax 5000-EC) for 1 min to crosslink 4M through radical polymerization to yield a patterned sample. The roll-to-roll imprinter and process is described elsewhere.[1]

Results and Discussion

Characterization of Dyneon™ FEP particle size and morphology was made by dynamic light scattering and SEM. Fig. 4 (a) shows the histogram of the statistics by number for 4 measurements and indicates that the dispersion is monomodal with polydispersity index of 0.052. This low polydispersity index indicates a narrow

particle size distribution making it almost monodisperse and will likely create a porous coating due to the fact that there are no small particles to fill up the voids between the larger particles. The mean particle size by intensity, number and volume are 141.8 nm, 118.1 nm and 141.7 nm, respectively. The SEM micrograph shown in Fig.4(b) of dried particles at 70°C indicates that they are spherical and homogeneous in shape.
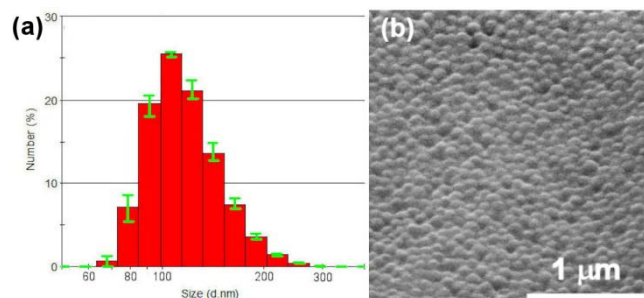

Fig. 4 (a) FEP particle size distribution statistics graph and (b) a representative scanning electron micrograph of the Dyneon™ FEP dry particles without sintering

Micron sized feature replication by Dyneon™ FEP particles was investigated by spin coating the as-received aqueous colloidal dispersion on a patterned silicon master to create a 3 micron coating. Water was then evaporated from the coating by heating on a hot plate set up at 70°C for 10 min. The dried patterned coating without sintering was carefully peeled off with a tape and imaged under SEM. Fig. 5 shows that the particles densely packed in the features and are capable of replicating complex multilevel geometries.
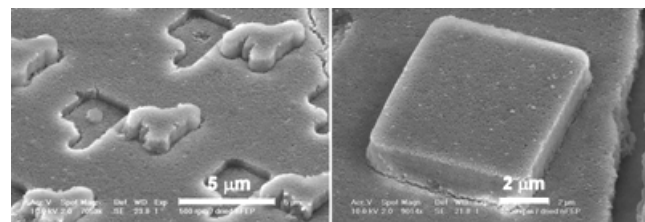

Fig. 5 Micron size feature replication by Dyneon™ FEP particles
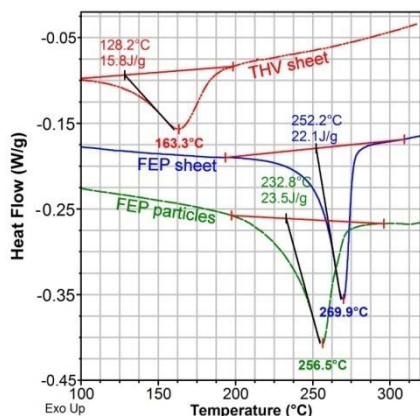

Fig. 6 DSC melting curves of Dyneon™ FEP particles, FEP sheet and THV sheet. The curves are onset along the ordinate.

The physical processes, which take place during sintering include melting of the polymer, coalescence of the particles, bubble removal and crystallization of the polymer. Surface area reduction (surface tension) is the driving force for sintering. Viscosity of the polymer in the molten state plays a significant role since viscous forces must be overcome in order to allow powder coalescence and crystallization of the polymer. Although the two processes of melting and sintering are strictly related, melting of polymers does not imply sintering of powders, unless adequately low viscosities are achieved. Too high a viscosity in the molten state generates a high fraction of pores entrapped in the molten mass.[20] Melting itself in the absence of pressure or force acting on the material is not necessarily accompanied by particle sintering, unless low viscosities are achieved. High loads during sintering causes the particles to deform leading to a decrease in porosity, therefore the load in this study was kept <200 psi. Differential scanning calorimetry (DSC) measurements were carried out on dried Dyneon™ FEP particles and FEP sheet to understand melting conditions. The results shown in Fig. 6 suggest that the melting temperature of dried Dyneon™ FEP particles is as much as 13°C below that of the FEP sheet. This decrease could be attributed to the small size effect and explained by the Thomson equation.[21,22] The increased melting range (width of peak) for the Dyneon™ FEP particles could be from the colloidal nature of the dispersion and the influence of foreign compounds such as emulsifiers and impurities. On the basis of the DSC data, the sintering temperature used in this study is between 200°C and 260°C.
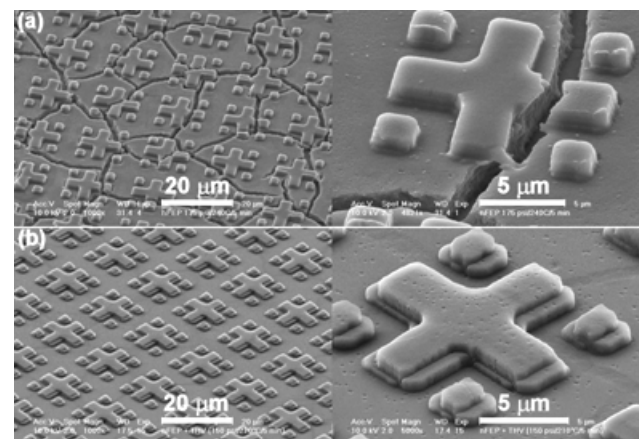

Fig. 7 Sintering of Dyneon™ FEP particles with (a) FEP and (b) THV backing sheets

The drying process during fabrication of stamps from pure Dyneon™ FEP latex created cracks as shown in Fig. 7(a). Formation of cracks during drying of hard particle latices with glass transition temperatures (Tg) above room temperature has been explained by others in terms of capillary forces experienced during drying[23] that depend on mechanical and visco-elastic properties of the matrix.[24,25] The first approach to heal the cracks was to adjust temperature and load during sintering. Temperature and loads greater than 270°C and 200 psi eliminated the cracks but particles highly deformed at these conditions and the desirable voids to increase gas permeability were eliminated.

The second approach to eliminate cracks was to flow a low melting temperature fluorothermoplastic, like THV, into the cracks. DSC measurements shown in Fig. 6 indicate that this material melts at a temperature of ~165°C. A stamp with Dyneon™ FEP particles and THV backing sheet was fabricated

by sintering at 210°C and 150 psi. Fig. 7 (b) shows that THV flowed into the cracks that were created during drying of Dyneon™ FEP particles and conformed to the 3D features in the silicon master. Higher magnification of the surface reveals presence of the desirable voids or pores.
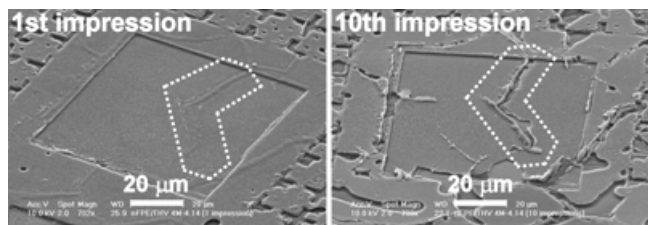

Fig. 8 Imprinted 4M with Dyneon™ FEP nanoparticles stamp with healed cracks by flowing THV

The next step was to fabricate a bigger stamp (~ 100 mm x 200 mm) and transfer it to an adhesive covered quartz roller for roll-to-roll imprinting of a web coated with 4M photopolymer. A quartz roller is used since the material stack deposited on the web to fabricate active matrix backplanes is opaque, requiring that the 4M photopolymer be UV exposed through the imprinting tool. Unfortunately, the interface of the healed cracks was not compatible with our imprint photopolymer and failed during roll-to-roll imprinting. Fig. 8 shows how the appearance of the imprinted 4M changed as the stamp aged. The dotted lines on the right image of Fig. 8 indicate the original location of the cracks. The left image of the figure shows the degradation of the repair after 10 impressions. The failure of the stamp material in these regions was caused by swelling during imprinting. It was not a surprise because THV swells ~20% by weight when soaked in acetone for 20 hours, whereas FEP does not absorb any acetone. It was very encouraging to see that the nanoparticles did not delaminate or deform during imprinting.

The next approach to eliminate cracks during drying was to add a coalescing aid (a volatile organic solvent [VOC]) to the dispersion that does not become part of the dried film. The solvent acts as a plasticizer, lowering the modulus of the particles in the dispersion so that they deform upon drying. Its main function is as the carrier for the non-volatile components and promotes polymer diffusion in the film.[26] The coalescing solvents investigated are 1,3-Dimethyl-2-imidazolidinone, Butyl Carbitol and TetraGlyme. 10% by weight of solvent was added to the Dyneon™ FEP dispersion. Non-patterned films were created by spin coating on silicon wafers and dried on a hot plate to evaluate efficiency on reducing crack formation. Inspection was carried out by SEM and is shown in Fig. 9. No reduction in crack formation was observed in the sample containing 1,3-Dimethyl-2-imidazolidinone. Butyl Carbitol is the most efficient coalescing solvent followed by TetraGlyme but >30% coalescing solvent is required to obtain a crack free coating.
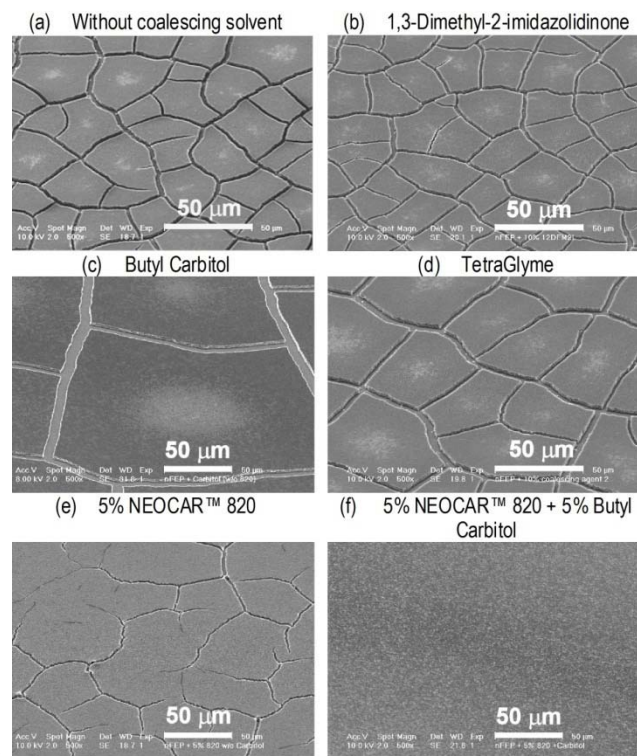

Fig. 9 Effect of coalescing solvent and low Tg latex additives on crack formation during drying of Dyneon™ FEP dispersions

Recent environmental requirements restrict the use of VOCs in coatings, and residual solvent can affect the sintering process. Therefore blends of high and low glass transition temperature lattices provide an interesting route to low VOC waterborne latex coatings for stamp fabrication. If the glass transition temperature of the latex particles is higher than the ambient temperature (hard particles), the final film was found to contain a large number of cracks in it, as observed with Dyneon™ FEP. Polymers with low glass transition temperatures (soft particles) will easily form a film at room temperature but the final film will be tacky with poor mechanical properties. In a latex blend containing soft and hard polymer particles, the soft particles deform to release capillary stresses during drying and the hard particles give mechanical strength and porosity to the final film.[27,28] Fig. 10 shows the elasticity and deformation of low Tg acrylic particles in a crack when mixed with Dyneon™ FEP. The amount of these deformable particles should be as low as possible to avoid filling of the desirable voids to improve gas permeability while preventing crack formation during drying. Fig. 9(e) shows that the width and number of cracks was highly reduced when a low Tg acrylic latex was added to the Dyneon™ FEP dispersion. The cracks were fully eliminated when both the soft particles and coalescing solvent were added as illustrated in Fig. 9(f).
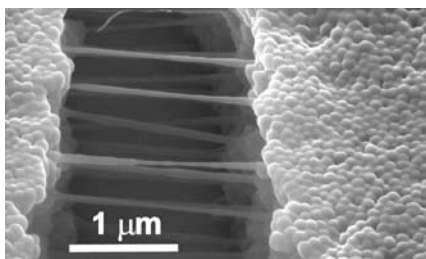
Fig. 10 Elasticity of low Tg latex when mixed with Dyneon™ FEP

The acrylic latex dispersions UCAR™ 627, UCAR™ 435 and NEOCAR™ 820 from Dow Chemical Company were investigated as deformable particles to release the internal stresses created during drying of Dyneon™ FEP dispersions. These materials were chosen because they have a pH near 9 that will have minimal effect on stability of Dyneon™ FEP dispersions and have glass transition temperatures below 25°C that will allow good film formation without cracks. UCAR™ 627 with a particle size of ~110 nm has great chemical and grain-crack resistance. UCAR™ 435 with a particle size of ~250 nm formulates into tough, flexible coatings and is crosslinkable to give a more durable coating. NEOCAR™ 820 with a particle size of ~70 nm is UV clear, cross-linkable and very hydrophobic. The three acrylic latex dispersions have carboxylic acid pendant groups, as indicated by their acid number in Table 2, which can be crosslinked to enhance durability, toughness and chemical compatibility. Therefore, 2.5% wt Carbodilite SV-02 crosslinker from Nisshinbo was added to the Dyneon™ FEP/acrylic dispersions.
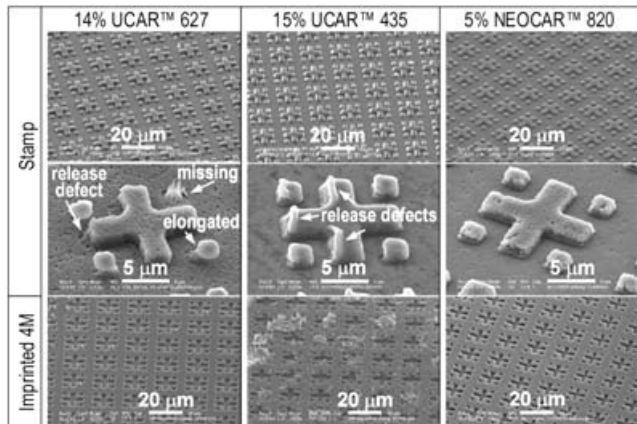

Fig. 11 (a) Stamps made with colloidal aqueous dispersions containing additives and (b) imprinted 4M with corresponding stamp

The optimum concentration of soft particles to obtain crack free coatings for Dyneon™ FEP dispersions containing 5% coalescing solvent was 14% wt for UCAR™ 627, 15% wt for UCAR™ 435 and 5% wt for NEOCAR™ 820. It may be seen in Fig. 11 that all these acrylic latices were effective at eliminating cracks. Embossed stamps were sintered at 240°C and 200 psi and released from the master at room temperature. Fig. 11 shows the stamp surface after release for each Dyneon™ FEP /acrylic latex formulation. UCAR™ 627 reduced the mechanical integrity of the stamp and some small features fractured and elongated during release from the silicon master. UCAR™ 435 showed plastic deformations or ridges in the release direction from the master

that can create grooves on the imprinted photopolymer and create problems during subsequent lithographic processing. NEOCAR™ 820 had good tear strength and great release properties.
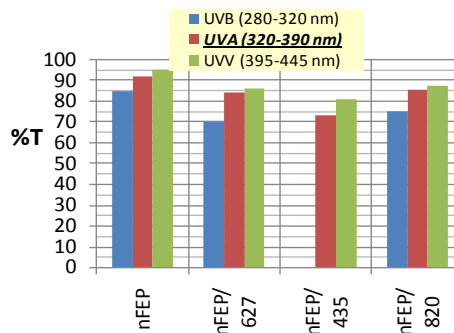

Fig. 12 UV transmission of Dyneon™ FEP stamps containing different acrylic latices

UV transparency of the sintered stamps was evaluated by measuring UV transmission through the stamps (Fig. 12). The UV wavelength required to cure 4M imprint photopolymer through the stamp is 320 to 400 nm; therefore it is desirable that UVA transmission be greater than 80%. UCAR™ 627 and NEOCAR™ 820 formulations had good UV transparency but UCAR™ 435 absorbed all UVB and UVA was below 80%.

Chemical resistance to 4M imprint photopolymer and release properties during hand imprinting were evaluated by curing 4M through the stamp and by imaging the imprinted surface of cured 4M with SEM. The UCAR™ 435 stamp was not compatible with 4M as some of the features highly adhered to the photopolymer and broke during release. UCAR™ 627 and NEOCAR™ 820 stamps released easily from 4M and no damage to the stamp was observed.
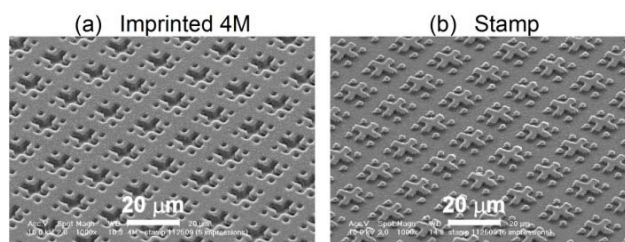

Fig. 13 Five imprints of 4M with stamp fabricated with Neocar™ 820/Dyneon™ FEP formulation

Dyneon™ FEP with NEOCAR™ 820 formulation offers great mechanical strength, high UV transparency and chemical compatibility with 4M imprint photopolymer. The next step was to determine if the stamp could withstand subsequent imprints. Fig. 13 shows the appearance of 4M and the stamp after 5 imprints using the same stamp of Dyneon™ FEP/NEOCAR™ 820 shown in Fig. 11. The features were preserved and no swelling or mechanical damage of the stamp was observed. The incorporation of the acrylic particles within the Dyneon™ FEP particles offers clear advantages in the fabrication of engineered stamps.
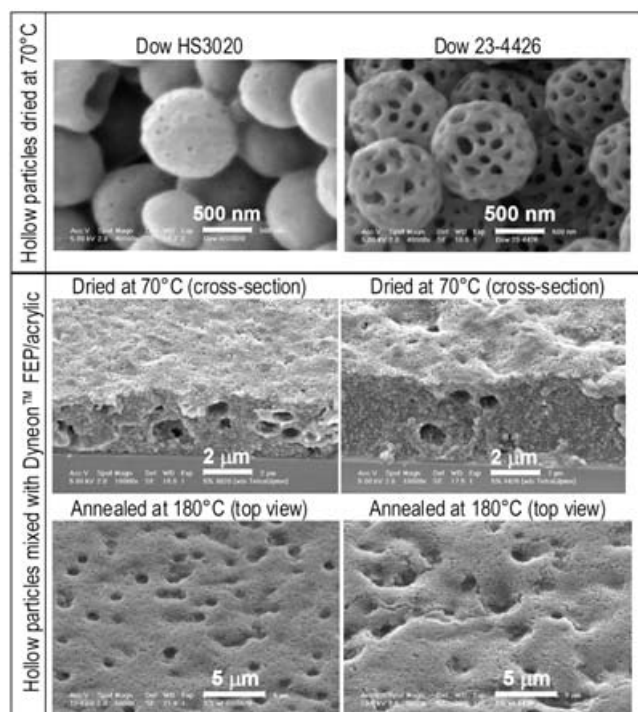
Fig. 14 SEM images of dry hollow polystyrene particles by themselves and mixed with Dyneon™ FEP/acrylic latex

Another approach to increase gas permeability was to introduce 1 micron voids in the bulk of the stamp by adding hollow particles with porous shells, filled with water, to the Dyneon™ FEP/acrylic latex dispersion. The idea is that as the coating dries; water vacates the latex, leaving air-filled 1 micron sized voids within each hollow particle. The pore microstructure of two different hollow polystyrene particle dispersions from Dow Chemical (HS3020 and 23-4426) was characterized by drying the as-received dispersion at 70°C and imaging under SEM. Surface pores of these particles are visible in Fig. 14 and show that HS3020 has bigger shell pores than 23-4426.

The next step was to add 5% hollow particles to Dyneon™ FEP/acrylic latex dispersion. The coatings were prepared by spin coating the dispersion on a silicon wafer and dried on a hot plate at 70°C followed by a 180°C anneal to check for structural stability of the hollow particles at high temperature. The coatings were cross-sectioned by fracturing the coated silicon wafer and inspected under SEM. The cross sections after drying at 70°C in Fig. 14 clearly show the presence of one micron voids in both samples demonstrating that the particles do not collapse during water evaporation and are compatible with the Dyneon™ FEP system. Unfortunately, no voids were observed in the cross section of the samples annealed at 180°C and the location of the hollow particles is evident on the surface by the presence of holes. It should be mentioned, that these holes were not observed on the surface of the samples after drying at 70°C. DSC measurements indicated that the dried hollow particles have a glass transition temperature of ~100°C with no melting peak observed below 300°C. These results prove that the particles collapsed during the high temperature anneal and did not melt. The factors that can encourage collapse in porous hollow latex are temperature, binder concentration, particle shell thickness and polymer modulus.[29] The successful use of this approach to create extra voids in the bulk of the stamp would require a fabrication process temperature below 100°C without any load. Other methods to generate this extra porosity include leachable additives such as sucrose, polyvinyl pyrrolidone, sodium diphenyl ether disulphonate and pH dependent soluble polymer latex.[30]

Future work includes optimization of latex dispersion formulation and sintering process to fabricate an engineered stamp with sufficient gas permeability that will not trap air bubbles in the photopolymer during the roll-to-roll imprint process and will have a life of ~1000 impressions. The testing to achieve this includes porosity and gas permeability characterization followed by roll-to-roll imprint life-testing of the stamp.

Conclusions

Self-aligned imprint lithography provides a means for fabricating active matrix backplanes on flexible substrates using continuous roll-to-roll processes. Soft molds made of plastics or elastomers casted on a silicon master have been used as stamps to pattern the 3D masks because of their low cost and ease of fabrication. This paper describes a novel and versatile method to fabricate porous stamps by using aqueous colloidal dispersions of tetrafluoroethylene-hexafluoropropylene copolymer (FEP) nanoparticles mixed with small amounts of soft acrylic particles and coalescing solvents. The basic idea is that the hard fluorinated particles, whose modulus is too high to deform during drying, remain as hard spheres and lead to a porous packing when drying is complete. Cracks created by capillary stresses during water evaporation are eliminated by adding soft particles and coalescing solvents to the latex formulation. The selection of the soft acrylic particles is an important parameter as it can affect mechanical strength, chemical compatibility, UV transparency and life of the stamp. One advantage of this process lies in the simplicity and flexibility of latex chemistry.

Acknowledgment

Notes and references

a *Phicot Inc., 1501 Page Mill Road, Palo Alto, CA 94304, USA. Fax: 650-857-7724; Tel:650-857-4348; E-mail:*
marcia.almanza.workman@phicot.com
b *Hewlett-Packard Company, 1501 Page Mill Road, Palo Alto, CA 94304, USA. Fax: 650-857-7724; Tel:650-857-4258; E-mail:*
carl.taussig@hp.com

1   A. Jeans, M. Almanza-Workman, R. Cobene, R. Elder, R. Garcia, R. F. Gomez-Pancorbo, W. Jackson, M. Jam, H.-J. Him, O. Kwon, H. Luo, J. Maltabes, P. Mei, C. Perlov, M. Smith and C. Taussig, Proc. SPIE, 2010, 7637, 763719.

2   H.-J. Kim, M. Almanza-Workman, B. Garcia, O. Kwon, F. Jeffrey, S. Braymen, J. Hauschildt, K. Junge, D. Larson, D. Stieler, A. Chaiken, B. Cobene, R. Elder, W. Jackson, M. Jam, A. Jeans, H. Luo, P. Mei, C. Perlov and C. Taussig, *J. Soc. Inf. Disp.*, 2009, **17**(11), 963.

3   W. B. Jackson, M. Almanza-Workman, A. Chaiken, R. Garcia, A. Jeans, H.-J. Kim, O. Kwon, H. Luo, P. Mei, C. Perlov, C. Taussig, M. S. Shur and A. Koudymov, *ECS Trans.*, 2007, **8**(1), 199.

4   H.-J. Kim and C. P. Taussig, C. P., US 7,718,077, 2010.

5   Z-M. Zhao, Y. Xia and G. M. Whitesides, *J. Mater. Chem.*, 1997, **7**(7), 1069.

6   K. M. Choi and J. A. Rogers, *Mat. Res. Soc. Symp. Proc.*, 2004, **788**, L9.6.1

7   Y.S. Kim, K. Y. Suh and H. Lee, *Appl. Phys. Lett.*, 2001, **79**(14), 2285.

8   Y. S. Kim, N. Y. Lee, J. R. Lim, M. J. Lee and S. Park, *Chem. Mater.*, 2005, **17**(23), 5867.

9   D.-G. Choi, J.-H. Jeong, Y.-S. Sim, E.-S. Lee, W.-S. Kim and B.-S. Bae, *Langmuir*, 2005, **21**(21), 9390.

10 B. K. Lee, L.-Y. Hong, H. Y. Lee, D.-P. Kim and T. Kawai, *Langmuir*, 2009, **25**(19), 11768.

11 J. P. Rolland, E. C. Hagberg, G. M. Denison, K. R. Carter and J. M. De Simone, *Angewandte Chemie*, 2004, **116**(43), 5920.

12 T. T. Truong, R. Lin, S. Jeon, H. H. Lee, J. Maria, A. Gaur, F. Hua, I. Meinel and J. A. Rogers, *Langmuir*, 2007, **23**(5), 2898.

13 S. S. Williams, S. Retterer, R. Lopez, R. Ruiz, E. T. Samulski, and J. M. DeSimone, *Nano Lett.* 2010, **10**(4), 1421.

14 D. R. Barbero, M. S. M Saifullah, P. Hoffman, H. J. Mathieu, D. Anderson, G. A. C. Jones, M. E. Welland and U. Steiner, *Adv. Funct. Mater.*, 2007, **17**(14), 2419.

15 S. H. Ahn and L. J. Guo, *Adv. Mater.*, 2008, **20**(11), 2044.

16 D.-Y. Khang and H. H. Lee, *Langmuir*, 2004, **20**(6), 2445.

17 D.-Y. Khang, H. Kang, T.-I. Kim and H. H. Lee, *Nano Lett.* 2004, **4**(4), 633.

18 C. Pina-Hernandez, P.-F. Fu and L. J. Guo, *J. Vac. Sci. Technol. B*, 2008, **26**(6), 2426.

19 C. Pina-Hernandez, L. J. Guo and P.-F. Fu, *ACS Nano*, 2010, **4**(8), 4776.

20 A. Greco and A. Maffezzoli, *J. Therm. Anal. Cal.*, 2003, **72**(3), 1167.

21 B. Siekmann and K. Westesen, *Coll. Surf, B: Biointerfaces*, 1994, **3**(3), 159.

22 H. Bunjes, M. H. J. Koch and K. Westesen, *Langmuir,* 2000, **16**(12), 5234.

23 C. J. Martinez and J. A. Lewis, *Langmuir*, 2002, **18**(12), 4689.

24 L. Pauchard, B. Abou and K. Sekimoto, *Langmuir,* 2009, **25**(12), 6672.

25 Q. Nawaz and Y. Rharbi, *Macromolecules*, 2008, **41**(15), 5928.

26 M. A. Winnik, *Curr. Opin. Colloid Interface Sci.*, 1997, **2**(2), 192.

27 S. Lepizzera, C. Lhommeau, G. Dilger, T. Pith and M. Lambla, *J. Polym. Sci. B,* 1997, **35**(13), 2093.

28 M. S. and W. B. Russel, *Langmuir*, 2005, **21**(11), 4938.

29 C. M. Cardinal, L. F. Francis and L. E. Sriven, J. *Coat. Technol. Res.*, 2009, **6**(4), 457.

30 I. C. Hodges, J. Hearn, and M. C. Wilkinson, *ACS Symp. Series*, 2001, **790**, 233.