Advances in Dryfilm Photoresist for Microfluidic Device Applications

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Abstract

A novel approach to form a 3 dimensional microfluidic device is demonstrated by the use of a customized negative dryfilm photoresist. The formation of the microfluidic chambers utilizes a lamination process, which enables the tenting of a negative photoresist onto the thickfilm barrier layer. Specifically in this paper, we will discuss the influences of the dryfilm photoresist components and how they relate to thermo-mechanical and adhesive properties required to form a microfluidic chamber.

Background

A common goal for inkjet technology has been increased print speeds and ultrahigh resolution. Historically, thermal inkjet manufacturers utilized a variety of materials and technologies to construct their nozzle plates, including metals and polymers (polyimide). Although these nozzle plate systems provided an increase in nozzle density and image resolution, in terms of drops per inch, there were many technical issues surrounding accurate alignment and bonding of the nozzle plate to its respective flow feature and/or heater chip. Thermal stresses/mismatch in subsequent process steps (i.e. thermal compression bonding and adhesive curing) can lead to an increase in swath expansion, feature misalignment, and ultimately print quality defects. Within the last 5 to 10 years HP and Canon, have independently developed and demonstrated the use of photolithography and microelectromechanical systems (MEMS) to construct nozzle chambers that realize the benefits of advanced photolithography equipment capable of achieving high resolution images and extremely accurate alignment

Photolithography equipment today has advanced in its ability to provide high resolution features with sub-micron alignment capabilities. In the early 1990's the first i-line (365nm) steppers were developed. These tools utilized lower wavelengths, and tighter filtered spectral outputs to improve image resolution [introduction to microlithography]. As projection steppers evolved towards lower wavelengths for reduced feature sizes (Moore's Law), photoresists were required to evolve as well. Therefore, the early 1990's also saw the birth of the chemically amplified negative resists photoresist [1, 2]

Traditionally, liquid photoresist are applied by a spin coating process onto a silicon wafer, then soft-baked (to elude the solvents from the resin). This process yields a very uniform resist film thickness across the wafer. Dryfilm photoresist lamination was introduced in the 1960's as an alternative coating process. Prior to the emergence of MEMs, the major market for dryfilm technology was primarily in the printed circuit board industry. In dryfilm resist applications, the photoresist is coated onto a carrier material (often with a release layer), softbaked (to drive off residual solvents), then spooled with an interleaf layer onto a core. Figure 1 is a cross-sectional view of a dryfilm on a carrier with a protective interleaf. While dryfilm processing may have eliminated the need for a spin coater, it is not without its own set of challenges specifically, (1) obtaining film in variety of thicknesses, and (2) poor thickness control.

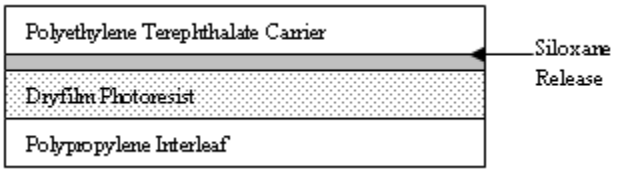


Figure 1. Typical construction of a dryfilm photoresist

Dryfilms are typically applied via a roll lamination system, which might controlled roller pressure, temperature, and speed. During lamination, the dryfilm is often heated above the resin's heat deflection and glass transition temperatures (HDT & Tg) enabling it to flow, and fill around the substrate's topography. A capable lamination process will insure that the dryfilm resist makes intimate contact with the substrate, displacing air and minimizing voids, in order to obtain the highest adhesion possible.

In this paper we describe a novel approach to forming a three dimensional chamber for an inkjet device utilizing MEMs technologies and a customized dryfilm photoresist. Additionally, we will present the results of our work customizing this negative resist formulation through (1) modeling of the lamination process, (2) optimizing thermomechanical properties for tenting applications, (3) maximizing interfacial adhesion.

Experimental

Materials

The customized dryfilm photoresist presented here was prepared by Engineering Material Systems Inc. (EMS) Delaware Ohio (US Patent application 20090155729). The dryfilm formulation utilized three resins including (1) a phenoxy resin (InChem Corp.) with a molecular weight of ~50,000 g/mol (2) a Novolac N695 resin (DIC Dainippon Ink & Chemical Co.) with a molecular weight of ~3000 g/mol, and (3) a naphthalene di-epoxy (DIC), which has a molecular weight of 271 g/mol. The photoacid generator used in this formulation is diaryliodonium hexafluoroantimonate supplied by Polyset Company Mechanicville, NY. Glycidoxypropyltrimethoxysilane silane was added as an adhesion promoter.

The liquid photoresist, described above, was coated onto a siloxane coated polyethylene terephthalate (PET) release liner,

dried via in-line ovens, and spooled with a polypropylene interleaf material. (See Figure 1)

Modeling

A finite element solver, Dyna3D by Livermore Software, is used to model the thermal mechanical process resulting in adhesion of PINP to flow feature layers. Boundary condition assumptions were minimized by using the full transient-dynamic and contact with thermal coupling capabilities of the software. The model domain includes a single chip from the wafer and corresponding section of the roller with symmetry conditions at the sectioned edges. Initially, the silicon and flow feature meshes are joined and are at the table temperature set point. The PINP and PET backing meshes are joined and at room temperature but are not yet in contact with the roller or flow feature meshes. The rubber roller mesh is initially at the elevated temperature and joined to a rigid armature that rolls about the roller axis and translates in the roller direction. Next, the roller lowers, develops a nip at the rubber / PET contact interface, then the roller translates and rolls at the prescribed velocity causing the PINP to contact and adhere to the flow feature layer.

Thermal Properties

Heat deflection temperatures (HDT) were measured using a Q400 TA Instrument thermal mechanical analyzer. 0.1N normal force was applied to the samples followed by a heating rate of 10.0C/min to 150C.

Q2000 MDSC was used to measure the various thermal transitions. Temperature scan of -90C to 250C at a rate of 5.0C/min was used for each sample.

Imaging: Absorption Coefficient

Varian/Cary UV-Vis spectrophotometer was used to obtain the absorption of the dryfilm from 280 to 650nm. Samples for UV-Vis analysis were prepared by laminating the dryfilm photoresist onto quartz microscope slides. Various thicknesses were obtained by laminating multiple film layers onto the quartz slides. The absorption coefficient was then calculated from laminated films with thicknesses of 1x (14μm), 2x (28μm), 3x (42μm) and 4x (56μm).

Adhesion Testing

The adhesive strength of the flow feature/nozzle plate interface was assessed via a Dage shear tester (Dage model 4000). In the Dage shear test, a series of 100um square structures are photolithographically imaged onto a Si wafer and a probe with a force gauge (BS250 cartridge) is used to shear the test structure from the underlying substrate (shear rate of 50 um/sec) while the failure force is recorded. Ten test mesas were sheared per location and the mean value of the maximum shear force reported.

Processing Equipment

Oxygen plasma surface treatments were performed in an M4L RF plasma unit at 300 Watts, for 3mins, with a 100sccm oxygen flow rate. After plasma treatment, a 1% glycidoxypropyl-trimethoxysilane adhesion promoter was applied to the flow feature surface on a CEE bench top spinner.

A Takatori ATM1100EF was used to laminate the dryfilm to a six inch wafer. The laminator has a roller pressure range of 0 to 0.3 MPa. The temperature range of the laminator for both the chuck and silicone roller is 20 to 150C.

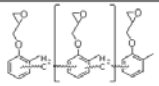
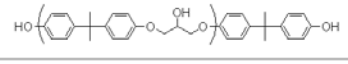
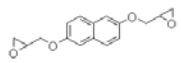
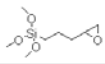
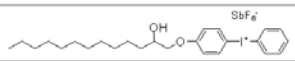
An Ultratech Prisma-ghi stepper was used for all resist imaging, including the 100μm square adhesion test structures. Post exposure bake processing was performed on a 100C hotplate for 10 minutes. The dryfilm photoresist was developed using cyclohexanone on a Tel Mark 8 coater/developer. After the post exposure bake, the photoresist was flood exposed with an OAI Model 2000 UV bump tool then place in a 175C oven for 2 hours to complete the cure process.

Results and Discussion

Dryfilm Formulation

In Table 1 below are the various components in the dryfilm photoresist formulation, their corresponding chemical structures, and purposes. Each resin was selected based upon its potential contribution to the dryfilm's performance in the areas of handling/film forming during manufacturing, thermomechanical properties, intrinsic adhesion, ink compatibility, and imaging.

Table 1. Constituent dryfilm resins

Material	Structure	Purpose
Dainippon N695		Film Formation Cross link density
Inchem PKHS-40 *(40% sol'n MEK)*		Film Formation
Dainippon HP-4032D		Cross link Density Plasticizer
Gelest SIG 5840		Adhesion Promotion
Polyset PC2506		Photoacid
BLO & MEK		Solvent

Thermal Analysis/Modeling

Typically, high molecular weight amorphous thermoplastic resins contain both a Tg and a HDT. In this application our dryfilm photoresist must maintain its resistance to flow in order to span across a 250 μm unsupported width. Meanwhile, the resist is also required to soften sufficiently in order to wet and conform to the underlying topography of the flow feature surface. Figure 2 is a cross-sectional view of the three dimensional chamber design with the chip, flow feature (ink barrier), and nozzle film layers. The thermal properties of the dryfilm have been designed to insure wide process window.

Shown in Table 2 are the DSC results spanning -90°C to 250°C. The coated dryfilm had a Tg of 22°C and the onset of thermal cure was 150°C. The low Tg insures the dryfilm photoresist will not be tacky at ambient FAB conditions.

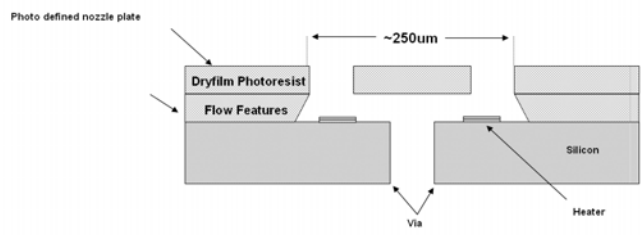


Figure 2. *Cross-sectional view of the micro-fluidic chamber*

Especially important to the lamination process, is the heat deflection temperature of the amorphous dryfilm resin system. The HDT is defined as the temperature at which a material will flow under an applied normal force. The slope of the deflection vs. temperature curve is especially important. If a material has a relative sharp negative slope the material will tend to flow readily which lead to more narrow lamination process window. This is common in low molecular weight resins and in crystalline polymers. Table 2 contains characteristic values for the Tg and HDT for the dryfilm resist as measured by TMA. With a HDT of 45°C, the dryfilm was able to conform well to the underlying flow feature surface while maintaining sufficient mechanical strength (aided by the PET carrier) to tent across a 250µm gap.

Table 2 Dryfilm photoresist thermomechanical properties

Thermal Analysis	Transition #1	Transition #2
MDSC	22C, Tg	150C, Onset of cure
TMA	25C, Tg	45C, Heat deflection temp

Based on the above dryfilm thermomechanical properties, material/lamination model was used to help define and predict the lamination process window as a function of process inputs.

The lamination model shows that, in the nip, at a roller speed of 2.29 mm/sec, the roller is in contact with the chip for 2.25 seconds. In that time, heat is transferred from the roller to the dryfilm as shown in Figure 3. This causes the dryfilm temperature to rise above the table temperature set point and soften in the rubber nip zone allowing the film to conform to the underlying flow feature topography. There is some thermal delay caused by the insulative PET carrier (the gap between lines AB and CD) but this can be controlled by varying the thickness of the PET. The heat transferred away from the roller surface during contact with the chip is recovered to after the nip is released (line A after 2.25 seconds).

The quality of the dryfilm resist lamination to the flow feature layer is determined, in part, by the lamination pressure which is monitored at points A (filter pillar), B (flow feature finger tip), and C (chamber region or valley) in Figure 4a. Under these conditions, the contact pressures at A, B, and C are very low relative to the roller nip pressure. Raising the roller temperature from 30C to 120C (figure 4b) results in increase in contact pressure at all points especially at point A which is the filter pillar contact.

As mentioned above, the increased temperature lowers the modulus of the dryfilm and PET carrier allowing better conformation to the flow feature topography. Increasing the nip pressure from 80KPa to 130KPa also increases finger and pillar contact pressure further and more uniformly (Figure 5a).

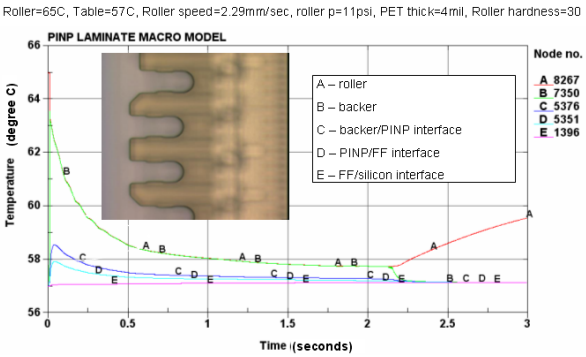


Figure 3 *– Transient thermal results for given table temperature and roller pressure condition.*

The underlying flow feature topography, which varies between 0.5 to 2 microns in the direction orthogonal to the flow feature surface, can substantially impact the uniformity of the pressure distribution. Figure 5b shows the improved uniformity in the pressure profile with a more planar topography.

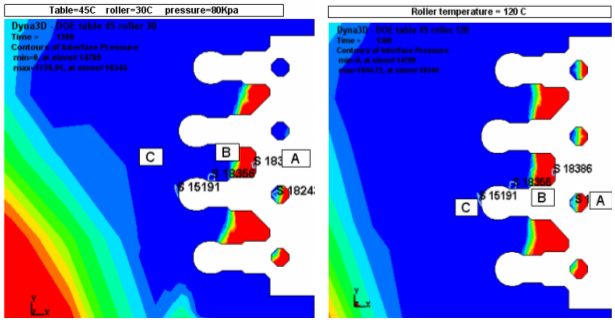


Figure 4a) *Lamination at control temperature, pressure and topography conditions showing pressure contact locations A, B, and C. 4b) Contact pressure with increased roller temperature.*

Adhesion

The ability to achieve and maintain adequate adhesion at the chip/flow feature and flow feature/nozzle plate interfaces is critical to the performance of an inkjet printhead. Adhesion relies to a great extent on both the properties of the materials to be joined and the preparation of those surfaces prior to coming into contact with one another. Some common methods used to enhance adhesion include oxygen plasma surface treatment, application of various silane chemistries, and combinations thereof. In addition, a reduced level of cure in the flow feature layer allows interfacial diffusion of unreacted epoxy groups from the uncured nozzle layer which then react during the final cure process to form an interpenetrating network that yields improved adhesion. This process is hereafter referred to as the "Co-bump and bake" process.

Both the maximum shear force and subsequent analysis of the failure interface yield important information about the quality of adhesion obtained. Further information regarding ink compatibility is gained by comparing the baseline adhesion value

to that obtained after immersing samples in ink over time at elevated temperatures.

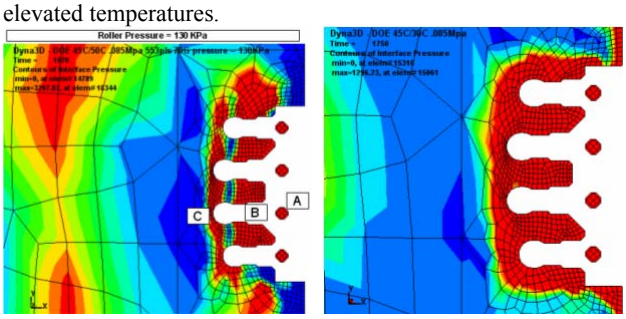


Figure 5a Lamination pressure profile in the nip at 130 KPa. 5b) Uniformity improvements due to a planar topography.

In Figure 6 below, the adhesive strength of the flow feature/nozzle plate interface is shown as a function of time in ink, and by process condition. The T0 value represents the adhesive force obtained immediately after lithographic processing. The T1 and T16 values were recorded after one week and sixteen weeks in ink at 60 degrees Celsius respectively. This data shows that while both an oxygen plasma surface treatment and silane application yield improved adhesion, the highest adhesive force was obtained by the Co-bump and bake process. This was true at both T0 and T16.

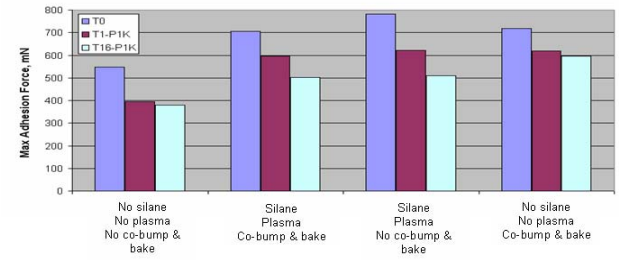


***Figure 6** Adhesion force as a function of time in ink at 60°C*

Dage Failure Analysis

The interfaces for the Dage shear test mesas were analyzed to determine the mode of failure with both optical (Nikon MM60) and scanning electron microscopes (Hitachi 3700S VP-SEM). Failure interfaces were characterized as either a) adhesive between the flow feature and nozzle plate, b) cohesive in the flow feature, or c) cohesive in the flow feature + adhesive at the chip/oxide interface. Representative failure interfaces are shown below in Figure 7.

The mode of the failure at the interface was found to be consistently predictive of the approximate adhesive force at failure and vice versa. At T0, the adhesion of the nozzle plate layer to the flow feature is at its maximum value. The interface shows that the flow feature material fails cohesively and is accompanied by an adhesive failure at the flow feature to Si/chip interface. As the samples are immersed in ink at 60C, the organic photoresist material swells and is plasticized. This process degrades the bulk resist properties (Tg decline) and the failure interface becomes predominately cohesive in the flow feature layer. As time progresses, the effect of the ink on the nozzle plate/flow feature interface is apparent in the progressive transition to an adhesive mode of failure. Figure 8 shows this transition for the sample that received an oxygen plasma and silane surface treatment.

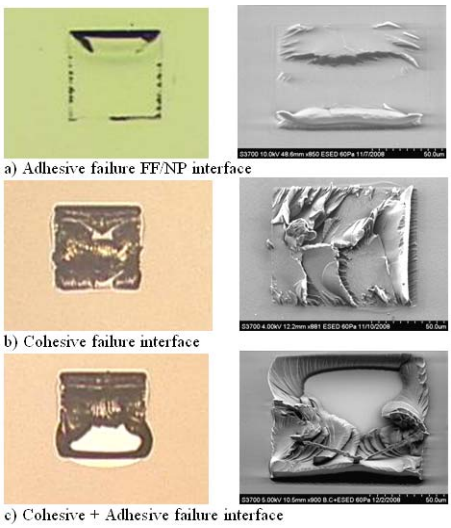


***Figure 7** Failure mode classifications for adhesion test structures*

***Figure 8** The transition from a cohesive to an adhesive failure mode with time in ink at T0, T1, and T16*

Summary/Conclusion

- The overall thermal properties of the dryfilm photoresist were influenced by the individual component resins. The high molecular weight phenoxy contributed to the high HDT of the dryfilm enabling a large lamination process window, while the HP4032D (a naphthalene based di-epoxy resin) provided lubricity and acted as a plasticizer increasing film flexibility and improving handling performance during processing.
- By incorporating the various thermomechanical properties into the Dyna3D, we were able to understand the lamination performance as a function of rate, pressure, roller temperature, wafer temperature and topography.
- Modeling was able to show the impact of the insulative properties of the PET on the conformance of the composite dryfilm to the chip/wafer topography.
- The interfacial diffusion process yielded the highest adhesion levels for T=0 and after 16 weeks in the presences of ink.

References

[1] L. Thompson, C. Grant, and M. Brown, Introduction to Microlithogrpahy (American Chemical Society, Washington DC., 94) pgs 1-15.

[2] K. Dietz, Dryfilm Photoresist Processing Technology (Electrochemical Publications LTD British Isles, 2001), pgs 1-28.