

Terefilm™ Photopolymer

MATERIAL GUIDE

Terefilm is a photopolymer which enables non-contact selective transfer of microelectronic devices from one surface to another with both accuracy and speed.

When used as a coating on a transparent donor substrate, Terefilm supports a Laser-Induced Forward Transfer (LIFT) process which can replace pick & place and elastomer stamping in demanding applications.

A wide variety of components, including ICs, passives and MicroLEDs can be placed at arbitrary pitches on display backplanes and other substrates.

Unlike elastomer stamps which pick up from a rigid substrate, Terefilm can pick up from flexible mediums such as transfer tape and other compliant materials.

Terefilm supports mass transfer and, because components are only released when exposed to light, the transfer of out-of-spec die can be blocked.

- **High Transparency – Light Transmission up to 90%**
- **Working Temperature up to 200° C**
- **Tunable to be photochemically activated at low energy and a variety of wavelengths**
- **Clean, residue free decomposition - Completely converted to gasses upon LIFT & bonding**

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APPLICATIONS

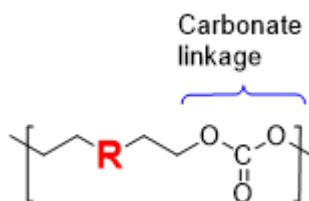
- **Mass transfer of ultra-small components such as MicroLEDs**
- **Mass transfer for die-to-wafer bonding**
- **Transfer of ultra-thin bare die for Flexible Hybrid Electronics (FHE)**
- **SiP and chiplet placement & packaging**

INTRODUCTION

This guide is an introduction to the Chemical, Physical, and working properties of Terefilm – a polycarbonate designed to facilitate fast and clean transfer of materials using Laser-Induced Forward Transfer (LIFT) principles.

CHEMISTRY

Polycarbonates are thermoplastic materials composed of hydrocarbon repeat units connected via carbonate-linkages, as shown below:



Where the R structure greatly influences mechanical properties, thermal stability, decomposition rate and byproducts, crystallinity, solubility, etc.

Terefilm was designed so that the chemical intermediates formed during non-oxidative decomposition are stabilized compared to traditional commercial polycarbonate materials, resulting in a much-reduced decomposition temperature (80 °C versus 200 °C).

When Terefilm is activated with a photoacid generator (PAG), the onset of decomposition is reduced by > 110 °C, which facilitates decomposition with gentle heating. Acid catalyzes degradation by protonating the carbonate-linkage, which then fragments into CO₂, water, and a volatile residue of the repeat unit, confirmed by TGA-GC-MS and TGA-FTIR analysis.

Formation and expansion of the gaseous products generates the force to push adhered components onto a target substrate without the surfaces being in intimate contact.

For applications that require ultra-fast decomposition, such as LIFT, appropriate choice of PAG is critical. It is recommended to use the PAG (4-Phenylthiophenyl)diphenylsulfonium triflate for these applications due to its excellent absorptivity in the UVA and UVB regions and its formation of the triflic superacid.

For other applications where slower decomposition is either desired or acceptable, weaker acids can be employed but higher heat and or/longer heating times will be required.

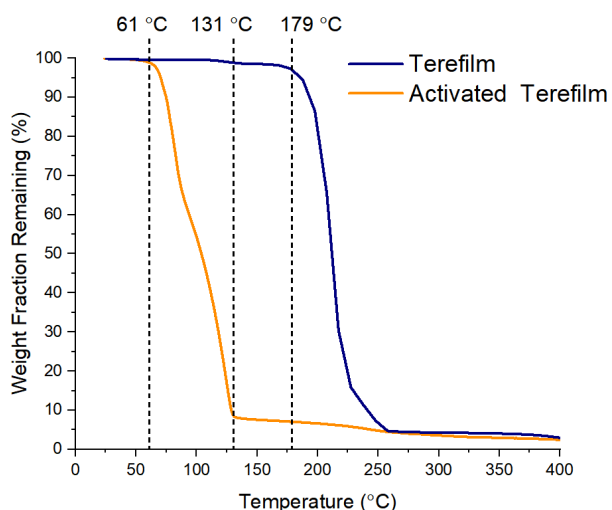


Fig. 1: TGA of Terefilm formulated with 3.5 wt% PAG before and after PAG activation with 311 nm irradiation (10 °C/min)

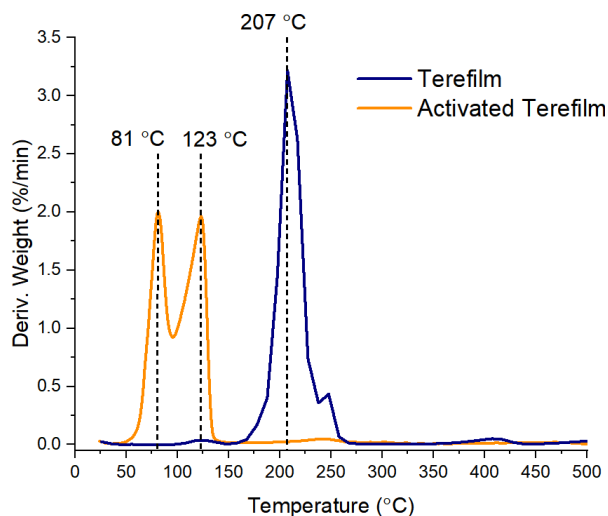


Fig. 2: DTG of Terefilm formulated with 3.5 wt% PAG before and after PAG activation with 311 nm irradiation (10 °C/min)

SOLUBILITY

Terefilm has excellent solubility in most organic solvents allowing for facile solvent processing of the material and removal from surfaces. The solubilities reported below were determined by the formation of clear solutions after sonicating sample for 60 minutes at 40 °C.

| Solvent | Solubility (wt%) * |
|---|--------------------|
| Acetone | ≥ 30 % |
| Acetonitrile | ≥ 30 % |
| Chloroform | ≥ 30 % |
| Dichloromethane | ≥ 30 % |
| Dimethylformamide | ≥ 30 % |
| Dimethyl Sulfoxide | ≥ 30 % |
| Ethyl Acetate | 10 % |
| Hexane | Insoluble |
| Isopropanol | Insoluble |
| Methanol | Insoluble |
| Propylene Glycol Monomethyl Ether Acetate | ≥ 30 % |
| Tetrahydrofuran | ≥ 30 % |
| Toluene | ≥ 30 % |
| Water | Insoluble |

* (polymer weight/solution weight) x100%

Table 1: Terefilm solubility in common solvents

THIN FILM PROPERTIES

DEPOSITION

Terefilm can be easily deposited as a thin film using any method of solvent casting. Terefilm films show excellent homogeneity, which is critical for uniform decomposition and lift-off force generation when activated by irradiation and/or heat.

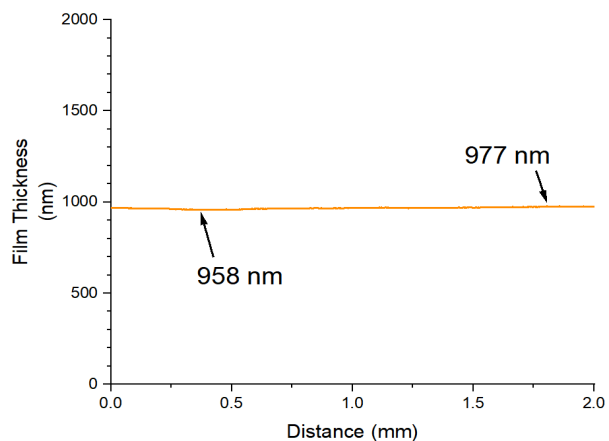


Fig. 3: (above) Profilometer trace and (below) AFM trace of Terefilm spin-casted onto fused-silica and a silicon wafer, respectively. Terefilm was formulated with 3.5 wt % PAG.

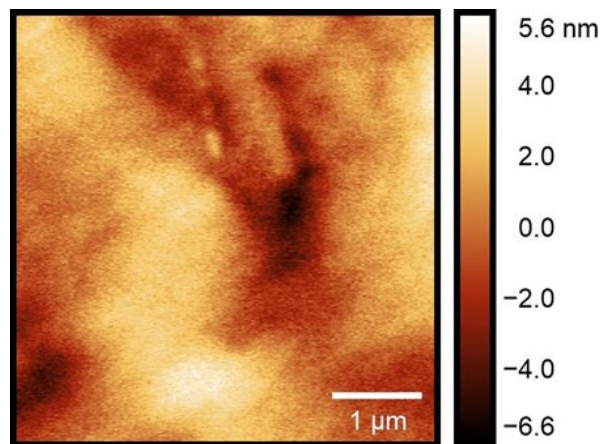


Figure 3 shows the uniformity and lack of phase-segregation in films composed without and with the (4-Phenylthiophenyl)diphenylsulfonium triflate PAG.

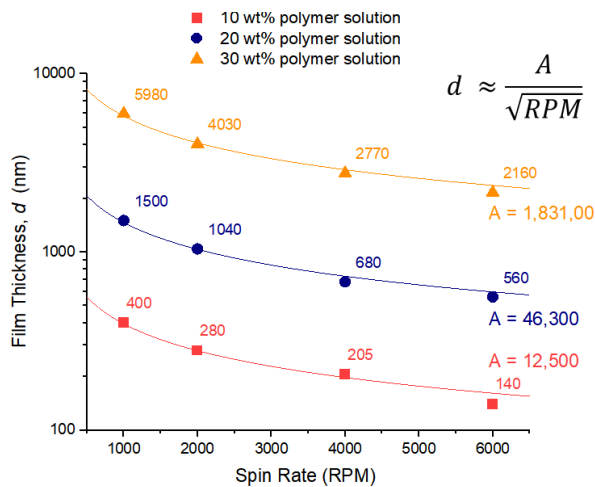


Fig. 4: Terefilm film thickness as function of spin rate and solution concentration.

Figure 4 shows a range of Terefilm thickness achievable through spin-coating. Films were prepared by sonicating the polymer in propylene glycol monomethyl ether acetate at either 10, 20, or 30 wt% for 60 minutes at 40 °C then filtered through a 450 nm nylon syringe filter. The films were deposited onto 5 mm diameter silicon wafers by dispensing 50 μ L of solution once the spin-coater attained the maximal spin-rate. In a typical procedure, the substrate is spun for 60 seconds after Terefilm solution deposition and then soft-baked at 140 °C for two minutes.

The figure also shows that film thickness (d) excellently correlates inversely with the square-root of the spin-rate. Although the proportionality constant (A) is calculated here, it highly depends on the exact conditions (e.g., solvent, deposition surface, substrate geometry, etc.) and should likewise be determined for each condition and spin-coater.

OPTICAL PROPERTIES

Terefilm is amorphous resulting in optically clear films, as determined from XRD, DSC, and the optical transparency of Terefilm coatings, which is essential for applications involving laser induced component transfer that require uniformly distributed irradiation intensity to facilitate a homogeneous rate of decomposition.



Fig. 5: Photo of a 2.3 μ m Terefilm film on an optically transparent fused silica disk.

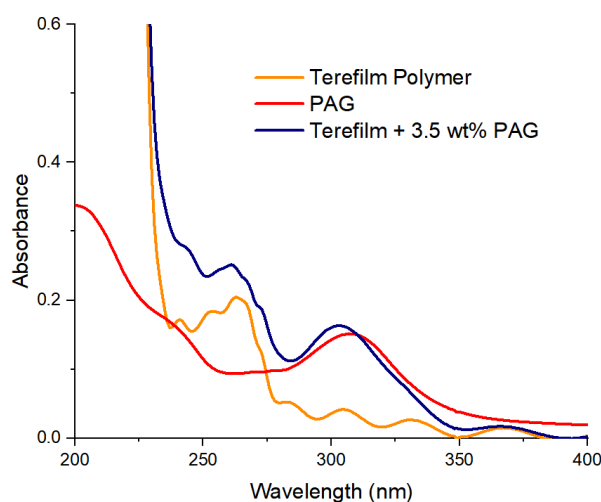


Fig. 6: UV-vis absorbance spectra of the Terefilm polymer, the PAG, and Terefilm PAG mix.

In Figure 6, absorbance of the Terefilm polymer is compared to the PAG (4 Phenylthiophenyl) diphenylsulfonium triflate and a Terefilm Mix of the Terefilm polymer with 3.5 wt% PAG. Samples were prepared as films on transparent fused silica plates. For laser induced transfer applications, UV-light in the absorption region of the PAG (290-340 nm) is used to activate the PAG and produce the catalytic acid. UV-light in the absorption region of the polymer (250-270 nm) is used to provide heat for the decomposition reaction. Table 2 lists the attenuation coefficients at several key wavelengths for the Terefilm polymer and Terefilm mix with 3.5% PAG.

| Selected Wavelengths | | | |
|------------------------|----------------------|-----------------------------|---|
| Film | λ_{max} (nm) | k (μm^{-1})* | Max thickness for $\geq 10\%$ transmittance (μm) |
| 266 nm | | | |
| Terefilm | 263 | 0.436 | 5.2 |
| Terefilm + 3.5 wt% PAG | 261, 303 | 0.509 | 4.5 |
| 308 nm | | | |
| Terefilm | 263 | 0.083 | 28 |
| Terefilm + 3.5 wt% PAG | 261, 303 | 0.342 | 6.7 |
| 320 nm | | | |
| Terefilm | 263 | 0.035 | 66 |
| Terefilm + 3.5 wt% PAG | 261, 303 | 0.237 | 9.7 |

*attenuation coefficient, k

Table 2: Terefilm optical properties

MECHANICAL PROPERTIES

For Terefilm applications involving the pickup of components onto a pre-casted Terefilm substrate, the mechanical properties like stiffness, adhesivity, T_g , and solid-liquid transition determine the processing conditions that facilitate high yield of component transfer onto the Terefilm sacrificial layer as well as strength of adhesion.

Terefilm is a hard, glassy polymer that is not inherently tacky and instead relies on the viscoelastic flow of the Terefilm polymer film around the components with adequate pressure and temperature. Once cooled, the polymer holds onto the component through Van der Waals interactions.

This process can be performed either above or below the polymer's T_g (125-140 °C). Above the transition, the pressure needed is minimal, while below the transition, the applied pressure and duration are greatly affected by the film's hardness.

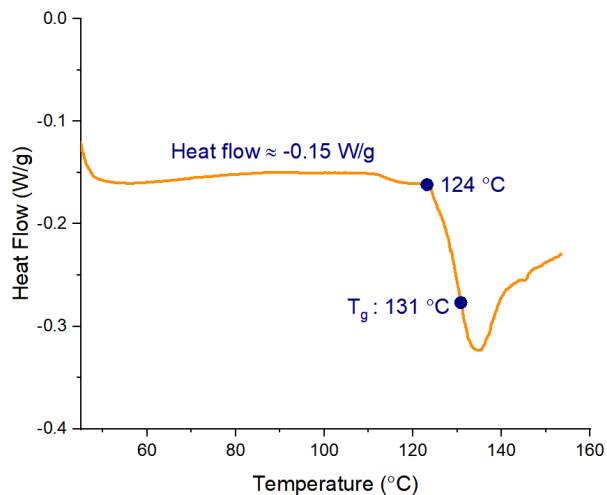


Fig. 7: DSC trace of Terefilm (20 °C/min).

Figure 7 shows the DSC trace of Terefilm. Terefilm has a single thermal transition that occurs 125 and 140 °C prior to the polymer's decomposition onset. When formulated with 3.5% PAG, the T_g is reduced by 5-15 °C due to plasticization.

| Temperature (°C) | Hardness (Gpa) |
|------------------|----------------|
| 35 | 4.6-4.8 |
| 45 | 4.4-4.6 |
| 55 | 4.3-4.5 |
| 65 | 4.2-4.5 |
| 75 | 4.1-4.3 |
| 85 | 4.1-4.4 |
| 90 | 4.2-4.8 |
| 100 | 4.3-4.4 |
| 110 | 4.0-4.1 |
| 115 | 3.9-4.1 |
| 120 | 3.8-3.9 |

Table 3. Terefilm hardness

Table 3 lists the hardness as a function of temperature for a 1 μm film of Terefilm, as measured by a nanoindenter.

AVAILABILITY

Terefilm is currently offered in evaluation quantities only and is not yet in general availability.

Terecircuits is working with select partners to develop LIFT-compatible production tools and additional applications for Terefilm. If you have a use case that could benefit from working with us, we want to hear from you!

Candidates will be evaluated based on market opportunity and experience working with similar materials and processes. Terecircuits may provide direct support for projects with the potential to solve unique market problems or where the partner can contribute significant resources in kind.

For other opportunities, limited quantities of evaluation materials may still be available. To qualify as an early evaluation partner, use the form at <http://terecircuits.com/contact/> and enter a brief description of your proposed project.

This version of the Material Guide is subject to revision as more use cases are added and data becomes available. Please use the above referenced contact form if you wish to subscribe to future updates.



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