

Excimer Laser Ablation of High Aspect Ratio Microvias Using a Novel Sensitizer-Enhanced Photopolymer

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Abstract—A new drop-in sensitizer has been developed for use with COTS negative tone photoresist to facilitate the laser fabrication of high aspect ratio microstructures in a thick film of photopolymer. Microvias with diameters as small as 50 μm have been successfully laser ablated in a 160 μm thick layer of the sensitized photoresist. Ablation rates of up to 86 nm/pulse have been achieved with an excimer laser.

Keywords—Sensitizer, laser ablation, negative tone photoresist, microvias

INTRODUCTION

Laser ablation of photopolymers is envisioned as a promising alternative to photolithography for micromachining small size features in photopolymers [1]. Soon after the introduction of this method [2], it became an important area of research [3]. With the increase in the feature aspect ratio (in the case of via holes, the feature aspect ratio is defined as the ratio of the hole's depth to its diameter), the traditional photolithography process used in some back-end operations is facing difficulties with dimensional precision, especially during the photoresist development step. These inaccuracies are most often manifested as deviations from cylindricity, typically as a highly conical shape of the microvia hole. When the aspect ratio becomes too high, the photoresist developer may not be able to completely dissolve the unexposed portion of the negative photoresist (or, in case of positive photoresist, the exposed portion) resulting in an incomplete via hole. These problems are more pronounced in the case of microvias, defined according to IPC-2226 as via holes with diameters of less than 150 μm and aspect ratios of up to 5:1 or more.

The problems with high aspect ratio (HAR) structures in photopolymers can be mitigated by using the laser dry etching technique [4], essentially, a laser ablation of the material as opposed to the wet etching method in which the excessive material is removed by the photoresist developer. It has long been established that laser ablation is a convenient and efficient method for micromachining precise features with

small sizes and high resolution in organic and inorganic materials [5, 6]. In the case of ablating polymeric materials such as the resists used in electronics manufacture, the low absorption coefficient [7], the material's carbonization [8], and debris contamination [9] on and around the ablated surface are some of the major problems associated with the process. Most of these problems are a direct result of using off-the-shelf materials designed for wet etching. To address these problems, novel photopolymers have been developed for laser ablation at a specific laser wavelength [10]. It is common knowledge in the industry that the synthesis of a new photopolymer formulation from scratch is a time-consuming and costly process. As an alternative approach, drop-in addition of a specially designed sensitizer to an existing photoresist formulation may provide a faster and more cost-effective solution.

THB151N (JSR Corp., Japan) is a negative photoresist that is extensively used for fabricating HAR microstructures. Such features require a thick layer of resists and THB151N provides these capabilities. For example, Rao et al. [11] demonstrated the possibility to spin-coat a 130 μm thick film with this photoresist. Thick photoresists such as THB151N are widely used in the fine-pitch flip-chip applications because they provide a suitable mold for electrodeposition of HAR metallic interconnects that allow the flip chips to be assembled to the substrate without underfill. There are other applications of this material such as the fabrication of microchannels [12], coils [13], cantilevers [14], sensors [15], and valves [16]. THB151N is easily strippable compared with another HAR material, the commonly used epoxy-based negative SU-8 photoresist.

The objectives of this work were to demonstrate a simple approach to modifying the off-the-shelf THB151N resist in order to improve its processability by increasing the absorption of UV laser irradiation, and to validate the use of the modified material in the laser fabrication of HAR microvias.

EXPERIMENTAL METHODS

A. Materials

9-Phenanthrol (9-Ph), monomethyl oxalyl chloride (MOC), tetrahydrofuran (anhydrous), and triethylene amine (TEA) were purchased from Sigma-Aldrich Corp. The THB151N photoresist was purchased from JSR Micro, Inc. The chemical composition of the as-received material included acrylic resin (35-45%), multifunctional acrylate (15-25%), and propylene

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glycol monomethyl ether acetate, PGMEA (30-40%). All materials were used as received.

B. Sensitizer Synthesis

The procedure shown in Fig. 1 was followed to synthesize the novel carrier gas sensitizer herein designated as 9-Ph-OX. 1.94 g 9-Ph, 1.22 g MOC (equimolar) and 4 g anhydrous tetrahydrofuran (THF) were charged into a flask in an ice/water bath with a magnetic stir bar. The amount of 1.5 g TEA was added dropwise into the flask, whereupon a white HCl-TEA salt forms. The reaction was allowed to proceed for 1 h with continuous stirring. The product solution was then filtered using filter paper to remove the HCl-TEA salt. The residual material left on the filter paper was washed with acetone three times. Then, THF and acetone were evaporated from the clear product solution to obtain the target product 9-Ph-OX, a dark reddish paste. Gas chromatography-mass spectroscopy (GC-MS) analysis was performed using an Agilent Technologies HP 6890 gas chromatograph coupled with an HP 5973 mass selective detector utilizing EI (electron ionization) with filament energy of 69.9 keV. The front inlet was in split mode with an inlet temperature of 250°C and a pressure of 8.24 psi, and the split ratio was 50:1. The initial GC oven temperature was 70°C for 2 min, and then the temperature was ramped to 300°C at a rate of 20°C/min and was held for 16.5 min. The total run time was 30 min. Separation was achieved on a ZEBRON ZB-35 capillary column operated in a constant flow mode with flow rate of 1.0 mL/min. The average velocity was 36 cm/s. The mass spectrometer was in scan mode with an m/z range from 10-800. The temperatures for MS source and MS quad were set at 230°C and 150°C, respectively. UV-vis spectra were obtained on a Varian Cary 5000 UV-vis-NIR spectrophotometer operating in absorption mode. The scanning rate was 600 nm/min and the scanning range was 200-600 nm.

The results from the GC-MS characterization of the synthesized novel carrier gas sensitizer 9-Ph-OX are shown in Figs. 2a (GC), 2b, and 2c (MS of 9-Ph and 9-Ph-OX, respectively). Fig. 2a shows two major solvent peaks below 5 min, the predominant 9-Ph-OX peak at 20 min (with target molecular weight of ~280 as shown in Fig. 2c) and the residual 9-Ph peak at 18 min (with molecular weight of ~194 as shown in Fig. 2b). It is clear that the synthesized product has high purity. Since the residual 9-Ph can still serve as a laser ablation energy absorber/sensitizer, no further purification was carried out to remove it. The UV-vis spectra of 9-Ph-OX and 9-Ph are shown in Fig. 3, which indicates strong absorption in the 248 nm range.

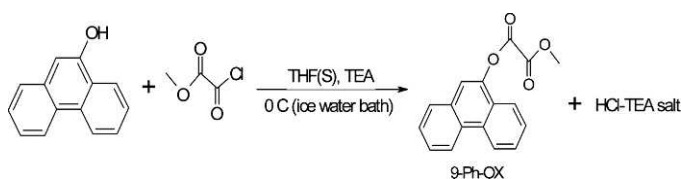


Fig. 1. Synthesis of the 9-Ph-OX carrier gas sensitizer.

C. Specimen Preparation

P-type silicon wafers of 200 mm diameter were used in this work. The wafers were cleaned in a piranha bath to remove organic impurities. After cleaning, the wafers were primed with hexamethyl disilazane (HMDS) to improve the adhesion properties. The modified photoresist was prepared by mixing 3% 9-Ph-OX with the as received THB-151N using acetone as a solvent. The resultant mixture was placed in ambient conditions for 24 h to evaporate all the acetone. The photoresist was spin-coated on the wafer using a SUSS RC-8 spincoater. The photoresist (4 g) was dispensed on the wafer

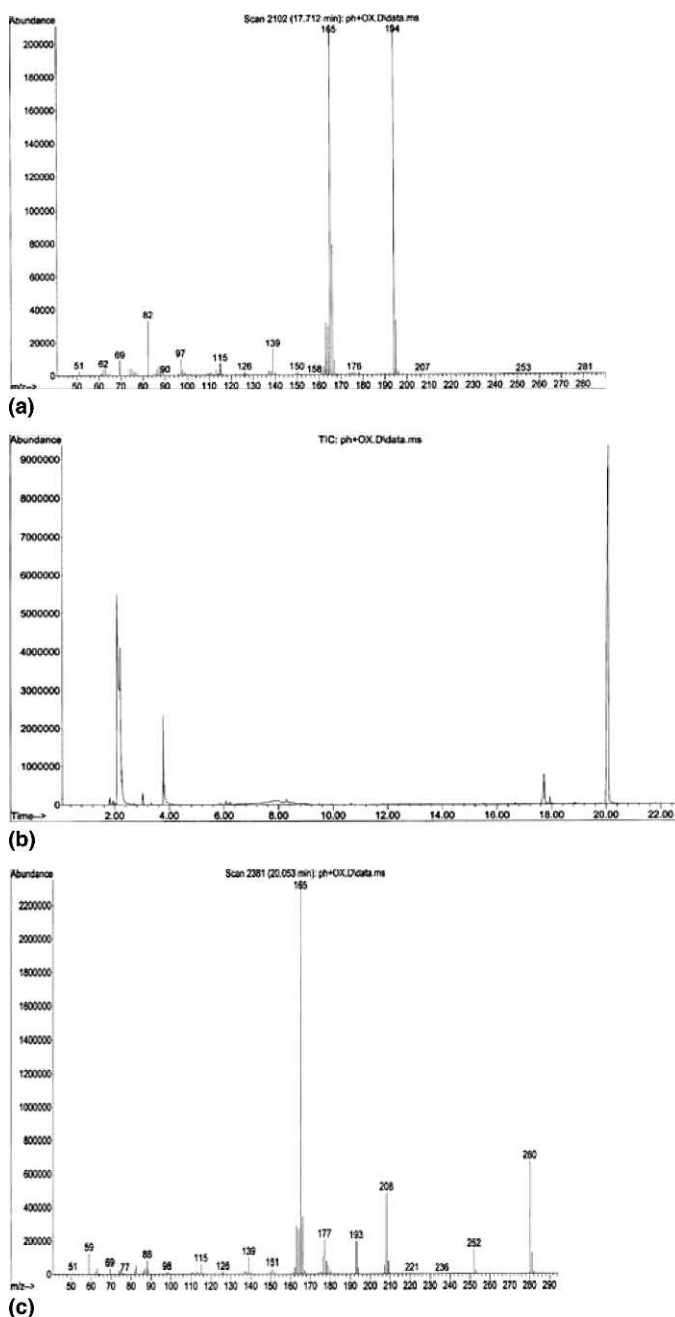


Fig. 2. (a) Gas-chromatography of 9-Ph-OX. (b) Mass spectra of 9-Ph. (c) Mass spectra of 9-Ph-OX.

in a 5-s cycle and then was spun at 700 rpm for 75 s. A uniform layer with a thickness of 160 μm in a double spin coating process on a 200 mm diameter wafer was achieved with these parameters.

After each spin coating cycle, the coated wafer was heated in an oven to 120°C and held at this temperature for 5 min to evaporate the solvent in the photoresist. The soft baking temperature was optimized (Table I) to maximize the hardness and adhesion of the primary layer. Another soft bake was performed after the secondary spin coating. After the second spin coating, the wafer was UV cured in a DYMAX 2000-EC UV curing system at 75 mW/cm² light intensity for 270 s.

D. Laser Ablation

The microvias were ablated using an Optec MicroMaster Excimer Laser Station. Excimer lasers are routinely used in various microfabrication [17], micromachining [18], and surface modification [19] applications. The excimer laser is very effective in polymer ablation due to the short pulse duration and high peak power (>10 MW) [20, 21]. The laser station in these experiments was equipped with a 248 nm ATLEX 300 SI short pulse excimer UV laser source and a three-element confocal UV micromachining module. The repetition rate could be varied from a single shot to 500 Hz. The laser station was equipped with real-time video capture software so that the ablation process could be monitored. The sample was mounted on X-Y translation stages equipped with a vacuum chuck.

The ablated vias were characterized by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX). The SEM images were taken using a JEOL JSM-

6490LV Scanning Electron Microscope. The EDX analysis was performed to analyze the debris found on the bottom of the microvias. The x-ray information of the debris was obtained via a Thermo Nanotracer Energy Dispersive x-ray detector with an NSS-300e acquisition engine.

RESULTS AND DISCUSSION

The experiments were carried out at laser fluences in the range of 15 mJ/cm² to 284 mJ/cm². The fluence was varied by adjusting the attenuation of the system. The laser ablation was carried out using a 50 μm diameter circular and 100 $\times$ 100 μm rectangular masks at 10 $\times$ demagnification and 50 Hz repetition rate. The ablation depth was measured with a TENCOR contact profiler after 1000 pulses. The fluence versus ablation depth graph is shown in Fig. 4. The curve does not show any abrupt threshold. This result supports the observation made by Kuper et al. [22] who stipulated that the longer wavelength excimer laser ablation curve is consistent with the thermal ablation model.

Examples of laser ablated microvias in the unmodified and modified resist are compared in Figs. 5a and 5b. The laser ablated microvias in the unmodified THB151N did not show very promising results. The microvias and trenches were conically shaped, the ablated surface was very rough, and the ablation rate was low (Fig. 5a). After modification of

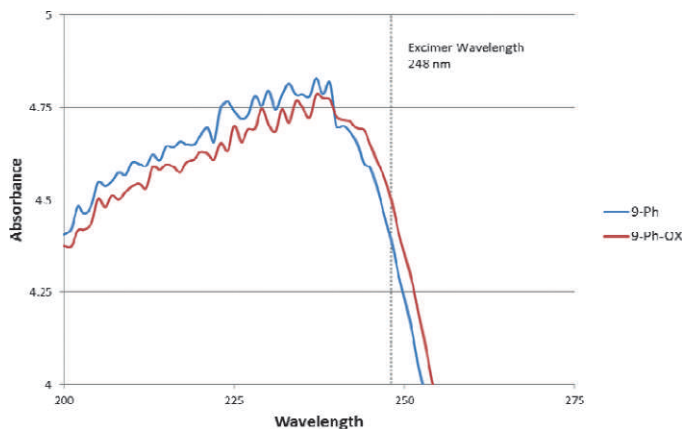


Fig. 3. UV-visible (UV-vis) spectra of 9-Ph-OX and 9-Ph.

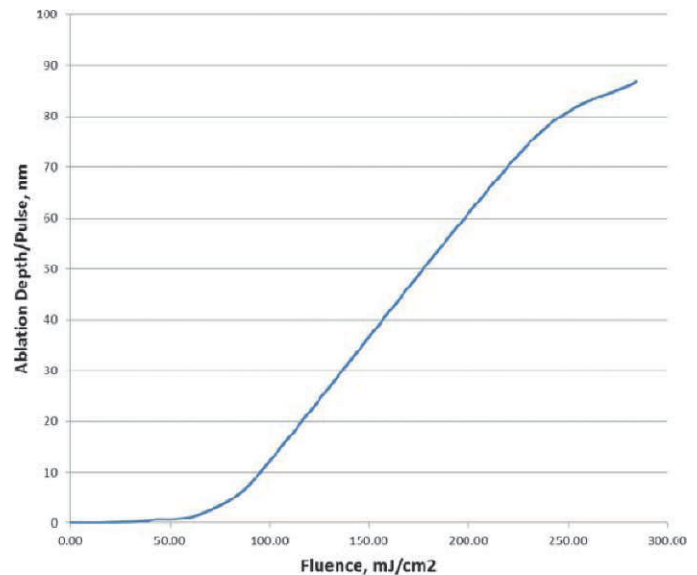


Fig. 4. Ablation depth per pulse for THB151N as a function of the incident excimer laser fluence.

Table I
Optimized Parameters for a Double Spin Coating Process

Layer	Dispense speed (rpm)	Dispense time (s)	Spin speed (rpm)	Soft bake temperature (°C)	Soft bake duration (min)	Average layer thickness (μm)
First layer	200	5	700	75	5	72
Second layer	200	5	700	75	5	160

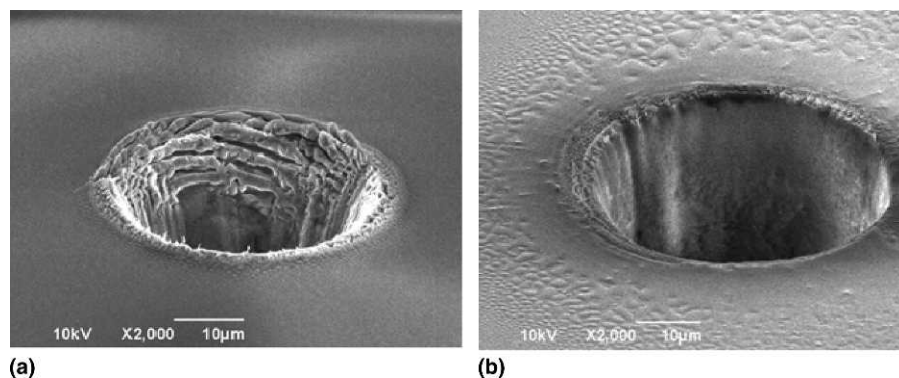


Fig. 5. (a) Laser ablated microvia in unmodified THB151N film. (b) Laser ablated microvia in modified THB151N film.

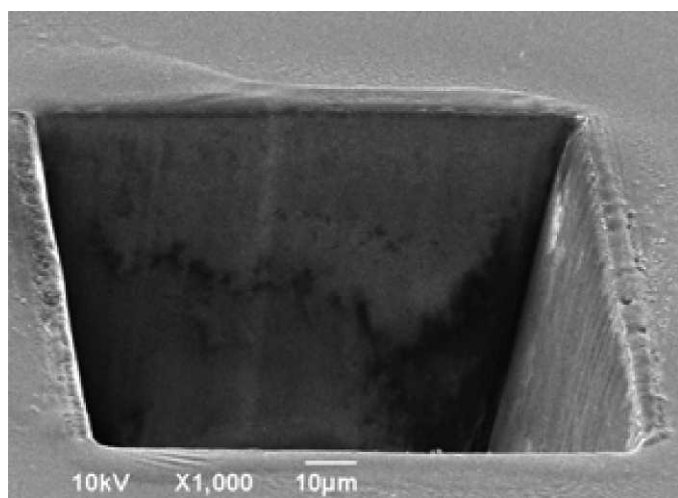


Fig. 6. A laser ablated rectangular pocket in the sensitizer enhanced THB151N film.

the THB151N with a 3% addition of the 9-Ph-OX sensitizer, the ablation rate showed significant improvement and microstructures with nearly straight walls were easily achieved (Figs. 5b and 6). The results are further compared in Table II.

The cross section of the microvia formed in the unmodified THB151N shows the deformation inside the microvia hole (Fig. 7a). The contrast with the cross section of the microvia in the modified THB151N is striking. As seen in Fig. 7b, the laser ablation of the modified resist produced nearly straight microvias with a smooth surface finish.

The most important criteria for successful laser ablation of polymers are the high absorptivity, existence of exothermic decomposition of the material, and generation of gaseous ablation products [13]. The faster and cleaner ablation of the drop-in sensitizer modified THB151N was attributed to the enhanced absorption at the incident laser wavelength at 248 nm due to the addition of 9-Ph-OX (Fig. 8). In addition, the new sensitizer is composed of an anthracene and oxalyl group that act as a UV laser energy absorber and carrier gas

Table II
Comparison of the Via Characteristics Formed by Excimer Laser Ablation in Unmodified and Modified Photoresist Layers

Repetition rate (Hz)	Fluence (mJ/cm ²)	Number of shots	THB151N, unmodified, top/bottom diameter (µm)	THB151N, modified, top/bottom diameter (µm)
50	182	6,000	49/20	50/49
		7,000	50/22	50/50
		8,000	50/25	50/50
		9,000	51/25	50/50
		10,000	51/26	50/50

generator, respectively. Previous research suggested that the oxalyl group combined in the photoresist photochemically decomposed into small molecule gases such as CO, CO₂, and CH₄, which eject out from the ablation spot with supersonic velocity carrying ablation debris away [23].

We observed traces of carbon-based debris on the surface, but corona treatment can remove them successfully. The laser-ablated microvias were successfully utilized as a mold in the process of copper electroplating used to stud bump the silicon wafer for flip-chip applications.

CONCLUSION

A novel sensitizer-modified THB151N photoresist was developed and tested for laser ablation of micro-sized features such as microvias as an alternative to the traditional photolithography process. The results were compared with unmodified THB151N photoresist. The sensitized photoresist showed a higher ablation rate than the unmodified THB151N and much better quality of ablation including higher dimensional and shape precision and smoother surfaces. The energy dispersive x-ray spectroscopy (EDX) inspection revealed the presence of a small amount of carbon residue on the bottom of the via holes. The debris could be cleaned with the use of, for example, corona treatment. The conclusion from the experimental results is that the modified THB151N resist is

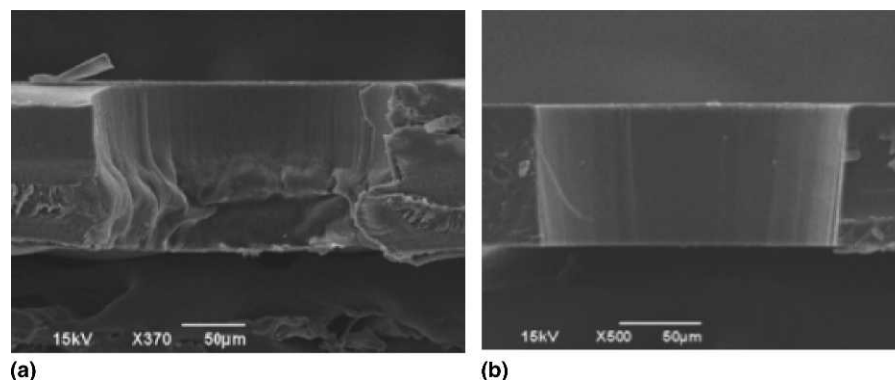


Fig. 7. (a) Cross section of the ablated microvia in unmodified THB151N film. (b) Cross section of the ablated microvia in modified THB151N film.

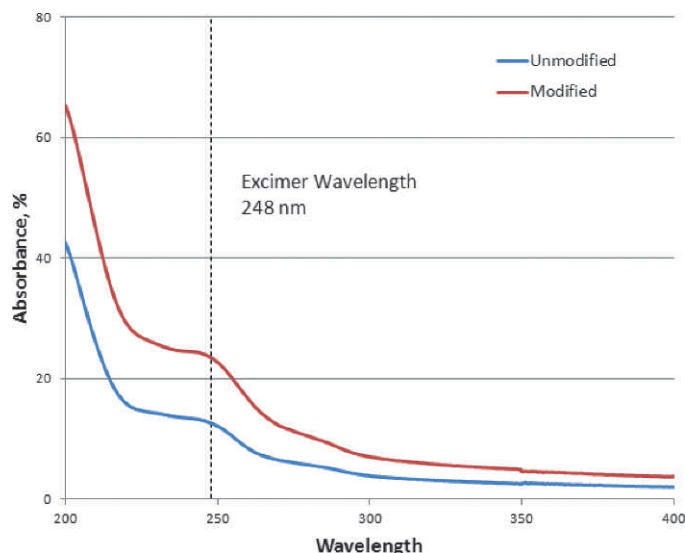


Fig. 8. UV-visible (UV-vis) spectra of modified and unmodified photoresist.

an excellent material for laser ablation of high aspect ratio microstructures, including microvias, in thick photopolymer films.

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