Poly(1,4-phenyleneazine *N,N*-dioxide): A Recyclable Material for a Solventless Laser-Imageable Resist Process

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Upon heating under vacuum, poly(1,4-phenyleneazine-*N,N*-dioxide) depolymerizes to give 1,4-dinitrosobenzene which can be condensed onto a suitable substrate. The nature of the condensate is dependent on the substrate temperature. At temperatures below −110 °C the condensate can be monomeric, at about −50 °C it is a mixture of dimer and oligomers, and at −20 °C it is polymeric. Thick and thin films of the polymer can be rapidly prepared by volatilization of 1,4-dinitrosobenzene from the bulk polymer onto a substrate and allowing the collected condensate to warm to room temperature. The resultant films appear to be stable indefinitely at room temperature and atmospheric pressure yet can be selectively removed from the substrate using a focused visible laser beam. After a suitable image-transfer process, the polymer is removed by heating to 100 °C. The laser imaging, deposition, and final removal of polymer are all nondestructive, thermal processes. Thus if a suitable vacuum chamber equipped with a cooling trap is used for this process, the polymer is 100% recyclable.

Introduction

Photoimageable polymers are of vital importance in the electronics industry for manufacturing circuit boards and computer chips. In a typical application the photoimageable formulation, or photoresist, is prepared by dissolving the polymer and photoactivating materials in a suitable solvent, coating onto the desired substrate, and then heating the substrate to drive off the solvent. The resultant photoresist film can be irradiated by a stationary source through a mask or exposed to a rapidly moving laser beam and then developed with a solvent which selectively dissolves the irradiated area to produce a circuit pattern in polymer. This pattern can be transferred to the substrate by typical metallization processes or reactive ion etching. Finally the polymer is removed by stripping with a solvent to leave the circuit pattern. Thus each step requires the use of large amounts of solvent: for the deposition, development, and final removal of film, for a process in which the polymer is impermanent. In addition to the cost of conventional solvent development for this process, there is the cost of disposal of the spent solvent-containing polymer at each step.

Approaches to imaging systems which do not require organic solvents include dry processing by direct-write e^- beam, which is a slow and expensive alternative to conventional resist processing, and the use of aqueous solvents that subsequently need to be treated to remove the polymer from spent solutions.[1a] For example, poly(methyl methacrylate) and poly(butene 1-sulfone) both depolymerize upon e^- beam exposure; however, solvent is often used for development because complete depolymerization requires high exposure doses.[1b,c] Ideally a process should use no solvent for preparing the polymer film, for imaging the polymer, and finally removing the polymer from the substrate. In this paper we describe a process whereby the polymer is deposited by chemical vapor deposition, directly imaged photothermally using a visible laser, and finally removed, after image transfer, by volatilization. The polymer used in this process, poly(1,4-phenyleneazine *N,N*-dioxide) (PNND), is completely recyclable.

Experimental Section

Preparation of Poly(1,4-phenyleneazine *N,N*-dioxide). A suspension of 1,4-benzoquinonedioxime (14.0 g) in water (100 mL) was stirred magnetically in a flask setup for steam distillation with a gas inlet in place of the steam inlet. The mixture was heated to 60–80 °C, and chlorine gas rapidly added. A green vapor volatilizes with the steam and condenses as a yellow solid into a receiver kept below 0 °C. The yellow solid (ca. 10 g) was filtered and immediately sublimed at 80 °C under vacuum (0.1 mmHg) onto a coldfinger cooled with dry ice/acetone. The sublimate was resublimed under similar conditions and was used without further purification. IR 3111, 1486, 1418, 1308, 1265, 1104, 1012, 859, 777, 570, and 485 cm^{-1} (lit.[3] 1481, 1411, 1304, 1265, 1100, 1010, 860, and 780 cm^{-1}).

CVD Films. PNND was added to the lower vessel shown in Figure 1. The 1 in. circular substrate (1,1,1-silicon, polished sodium chloride or polished quartz) was firmly attached to the flat bottom of the coldfinger by spring clips and gallium was placed between the coldfinger and the substrate to improve

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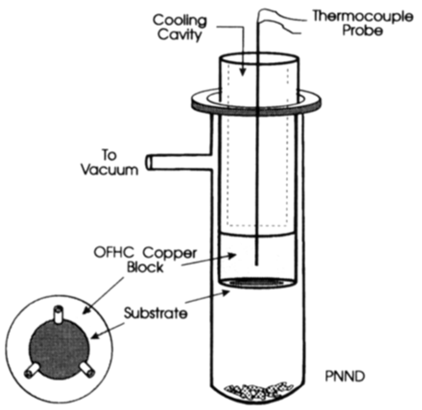


Figure 1. Chemical vapor depositon (CVD) apparatus. During deposition the cooling cavity is cooled with ice or dry ice, and the lower part of the vessel is immersed in a thermostated oil bath. To recycle PNND to the feedstock, the cooling cavity is heated by inserting cartridge heaters and the lower vessel is cooled in a dry ice/acetone bath. (OHFC copper is oxygen-free high-conductivity copper.)

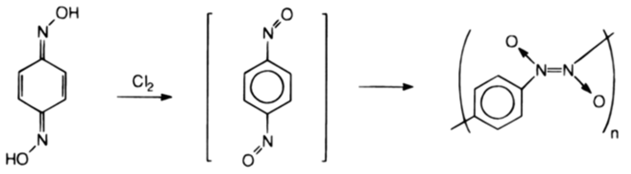
thermal conduction for some experiments. The apparatus was evacuated to <0.01 mmHg, and dry ice and acetone were added to the coldfinger. The lower part of the vessel was then heated in a thermostated oil bath, after 1−10 min the oil bath was removed, and then the coolant was removed from the coldfinger. When the whole apparatus reached room temperature, the vessel was brought to atmospheric pressure and the coated substrate was removed. At this point the coldfinger and the higher points of the lower part of the vessel were coated with condensed polymer. The vessel was evacuated and the lower part of the vessel containing the feed polymer was cooled in a dry ice/acetone bath. The coldfinger was then warmed with cartridge heaters, and higher points of the vessel were heated with a hot-air dryer. The polymer then condensed in the lower part of the vessel with the feed polymer where it was used to further CVD experiments.

Direct-Write Laser Imaging. Direct laser writing to form micron-sized patterns was achieved with the TEM$_{00}$ mode of an argon ion laser (Spectra Physics Model 22−05) operating at 514 nm. The beam was expanded (3×), collimated with a telescope, and focused through a microscope objective (0.2 NA). The measured beam diameter is approximately 9 ± 1.0 μm at 1/*e* intensity points and was roughly Gaussian. Laser powers between 35 and 350 mW were used to create lines in thin films of poly(1,4-phenyleneazine *N*,*N*-dioxide). The laser beam was focused onto the polymer-coated substrate that was attached to a PC-controlled motorized $x-y$ stage. Scan velocities of the substrate from 1 to 750 μm s^{-1}, the limit of the motorized stages, were utilized for forming patterns in the resist layer. For complete removal of thick films (2−6 μm), several repetitive scans may be required. Patterned films can be formed by raster scanning the focused beam rather than the substrate. The uniformity of the CVD films was measured by optical microscopy by focusing on the substrate in the lines in the patterned polymer at numerous points across the film and by comparing the depth change versus focusing on the polymer surface. In addition samples polymer samples were scratched with a sharp point and the depth of the scratch measured on a Tencor profilometer. The uniformity of the 1 μm films was within 5%.

Results

Poly(1,4-phenyleneazine *N*,*N*-dioxide) (PNND) is readily prepared from the addition of chlorine to 1,4-benzoquinonedioxime (Scheme 1).[2] It was previously reported that this material sublimes by heating under vacuum to given a green solid which on warming above 0 °C turns yellow and repolymerizes.[2,3] A detailed spectroscopic study of this reaction has been reported elsewhere.[4] Films of PNND were deposited onto various substrates (quartz, sodium chloride, and silicon) using the modified sublimation apparatus shown in Figure 1. The 1 in. diameter substrate can be attached to the “coldfinger” which can be cooled to temperatures between −70 and 0 °C during the film preparation and then heated, after the substrate is removed, to volatilize the excess polymer back to the cooled feedstock vessel for recycling between depositions. There appeared to be no fatigue in the polymer from recycling; approximately 50 CVD experiments have been run on the same sample of PNND over a 1−2 year period. Thus films of PNND were prepared by chemical vapor deposition (CVD) by heating the feed polymer at temperatures up to 80 °C under vacuum and cooling the substrate on a modified “coldfinger”, at 0 °C or below, and then warming the cold finger to room temperature. Film thicknesses from 0.3 to 40 μm of the CVD polymer were obtained in relatively short deposition times of 1−10 min. Film thickness was dependent on both sublimation temperature and pressure, and uniform 1 μm films were routinely deposited during 10 min at about 40 °C at 0.01 mmHg pressure. The infrared spectrum of a CVD film of PNND on sodium chloride is shown in Figure 2. The *trans*-O—N=N—O stretching frequency at 1265 cm^{-1} confirms the azine di-*N*-oxide structure and agrees well with other reports for PNND.[2,3] The UV absorption spectrum shows a broad featureless absorption from 200 to 470 nm with broad absorption shoulders at 250 and 390 nm (Figure 3). The resultant films were inert to organic solvents, aqueous bases, and acids with the exception of concentrated nitric acid. Although the CVD films were chemically inert, they were readily removed from the substrate by placing on a hot plate heated to above 100 °C at atmospheric pressure, or under vacuum, for about 10 min.

Scheme 1. Synthesis and Polymerization of 1,4-Dinitrosobenzene



CVD films prepared by this method were exposed to a focused laser beam ($\lambda = 514$ nm). The sample was moved through the focal spot of the laser beam on a controlled $x-y$ stage. Figure 4 shows clean, selective patterns with line widths (ca. 10 μm) similar to the size of the focal spot of the laser beam, rapidly written at velocities up to 750 μm s^{-1} in both thin and thick films. The lines showed no evidence of debris or fallout, by optical microscopy, that are commonly observed with other laser processing techniques such as laser ablation.[5] Finally the imaged polymer is removed from the substrate simply by heating on a hot plate for 10 min.

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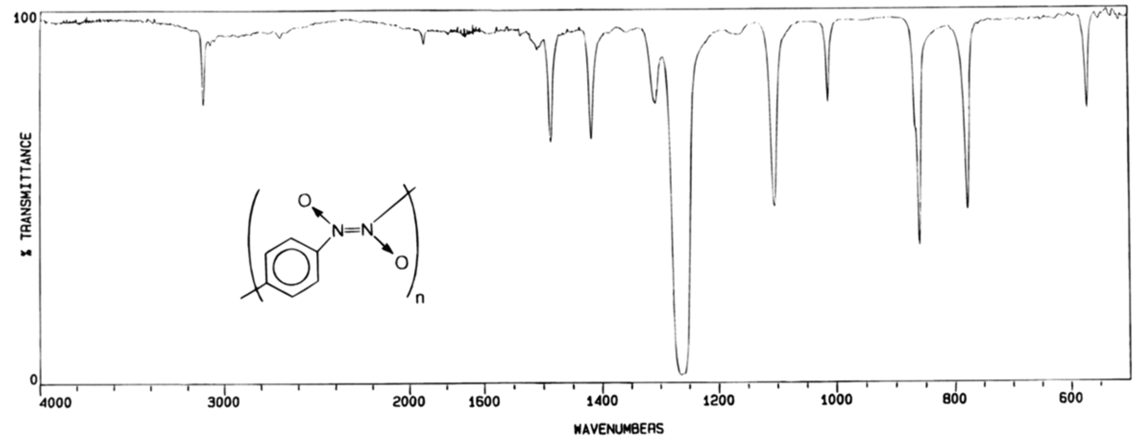

Figure 2. IR spectrum of CVD film of poly(1,4-phenyleneazine *N,N*-dioxide). (Note scale change at 1600 cm^{-1}.)

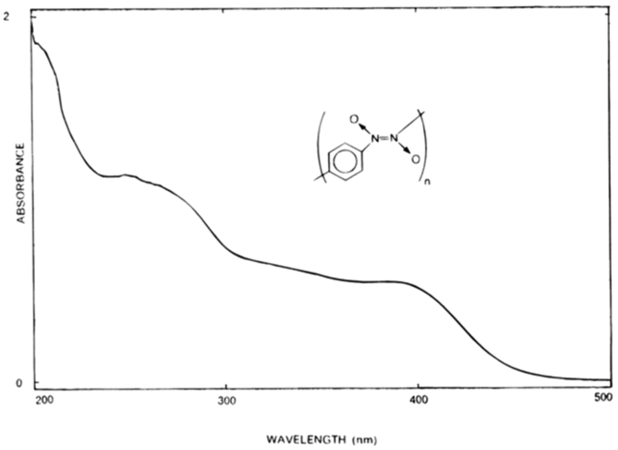

Figure 3. UV absorption spectrum of CVD film poly(1,4-phenyleneazine *N,N*-dioxide).

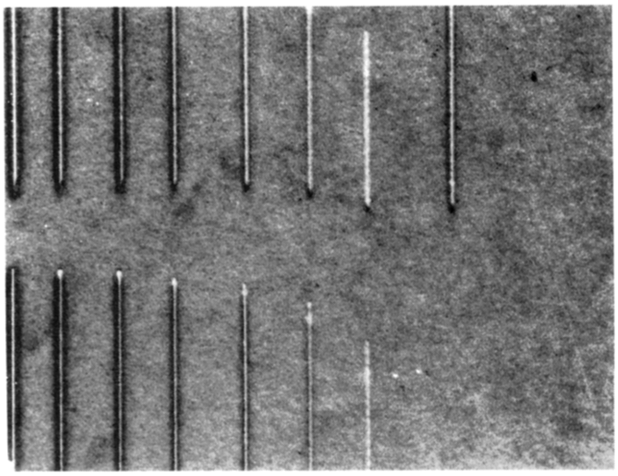

Figure 4. Optical micrograph of laser patterned lines in 1 μm thick film of poly(1,4-phenyleneazine *N,N*-dioxide). The lines are roughly 10 μm in width and were formed from a focused argon ion laser operating at 514 nm. The top lines were drawn with 250 mW power and scan velocities (left to right) of 5, 10, 20, 50, 100, 200, 500, and 100 μm s^{-1}. The bottom lines were drawn with 200 mW power and scan velocities (left to right) of 5, 10, 20, 50, 100, 200, and 500 μm s^{-1}.

Discussion

PNND undergoes CVD under very mild conditions (<80 °C), is impermanent, and is also laser imageable. CVD polymers have been prepared from suitable monomers under harsh thermal conditions: [2.2]paracyclophane and dispiro[2.2.2.2]deca-4,9-diene polymerize on substrates heated to 600 and 450 °C, respectively.[6,7] The properties of PNND are derived from the unique chemistry of aromatic *C*-nitroso compounds. *C*-Nitrosoarenes generally exist as dimers in the solid state and may be converted to the respective monomer upon heating.[8] The structure of the dimer has been characterized as *cis*- or *trans*-dinitrosophenyleneazine *N,N*-oxides.[8] The propensity for *C*-nitroso groups to associate with each other is known for compounds which contain more than one NO group. For example, 1,2-dinitrosobenzene can be isolated in the solid state only at temperatures below −190 °C and cyclizes to form benzofuroxan at higher temperatures.[9] 1,3- and 1,4-dinitrosobenzene exist as polymers and dinitrosocyclohexanes exist as oligomers in the solid state at room temperature.[3,10] 1,4-Dinitrosobenzene undergoes the following transformation upon heating from cryogenic temperatures:

$$\underset{-240\ ^\circ\mathrm{C}}{\text{monomer}} \xrightarrow{-90\ ^\circ\mathrm{C}} \underset{-90\text{ to }-50\ ^\circ\mathrm{C}}{\text{dimer (+oligomer)}} \xrightarrow{-50\text{ to }-10\ ^\circ\mathrm{C}} \underset{-10\text{ to }+100\ ^\circ\mathrm{C}}{\text{polymer}}$$

Furthermore it is known that heating the polymer to 80 °C under vacuum and collecting the condensate at −240 °C gives 1,4-dinitrosobenzene; therefore, 1,4-dinitrosobenzene can exist in the gas phase.[4] Thus, the activation energy for formation of both nitrosoarene and polymerization of nitrosoarene is low. An activation energy of 20 ± 2 kcal mol^{-1} was reported for monomer formation from solution studies on the dissociation of cis and trans dimers to *C*-nitrosobenzenes.[11] The tautomerization of benzofuroxans involves dissociation and association of a *C*-dinitrosobenzene and has an activation energy of 15 ± 1 kcal mol^{-1}.[12] Dimerizations of *C*-nitroso compounds have activation energies of 9 ± 2 kcal mol^{-1}.[13] Thus the CVD process for preparing the films is depolymerization of the polymer upon heating

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to give monomer vapor which condenses on the coldfinger as a mixture of dimer and oligomers. Warming the coldfinger to room temperature completes the polymerization reaction. The CVD films are very stable at atmospheric pressure because the activation energy for O—N=N—O bond cleavage is higher than C—NO dimerization. Also, for a monomer unit to be removed from the polymer by volatilization requires simultaneous cleavage of two O—N=N—O bonds on the same aromatic unit in the polymer chain, making volatilization at room temperatures less likely. While there are earlier reports that the chemical integrity of the polymer changes with time and because of our own observation that a sample of commercially available "1,4-dinitrosobenzene" is intractable, the material prepared for our experiments has had a useful lifetime of more than a year without fatigue.[14] Thus, the stability of the CVD films at atmospheric pressure and at temperatures below 100 °C is an example of Le Chatelier's principle.

The laser patterning of the sublimed polymer occurs via localized heating of the polymer and underlying substrate. The UV absorption spectrum of the polymer (Figure 3) shows no absorption at 514 nm and attempts to image the polymer by irradiation with a Hg/Xe lamp through a mask have so far been unsuccessful, i.e., the polymer is photochemically inert. The laser imaging process can be carried out under vacuum or in an ambient environment. Thus the laser heats the substrate and polymer, which thermally decomposes to monomer and volatilizes from the substrate. Laser ablation can be used to image polymers but usually requires deep UV light (<300 nm) and high laser power.[5] It is unlikely that ablation is the mechanism for PNND imaging as the polymer is rapidly imaged using long-wavelength light and quite low laser powers.

The advantages of the imaging process with PNND versus the wet process are shown in Figure 5. The wet process requires separate tools or equipment for six of the seven steps: preparation of the formulation, spin coating, baking, imaging, development, metallization or etch, and resist strip. In contrast the dry process requires only four steps. In addition, while we have conducted our laboratory CVD and laser imaging experiments separately, it should be possible to design a single cell for both CVD and laser imaging. Also for the CVD, laser imaging and stripping steps, the polymer is converted to monomer which repolymerizes, i.e., the material is not destroyed or converted to a different chemical moiety. Thus the material is completely recyclable. Finally the need for solvent is eliminated using the PNND process.

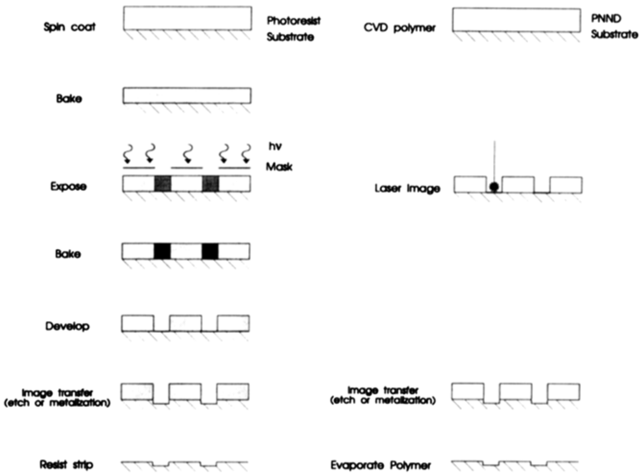

Figure 5. Schemes for conventional wet processing of a photoresist (left) versus dry processing (right) with poly(1,4-phenyleneazine *N,N*-dioxide).

Conclusion

PNND is a polymer that is inert to solvents, acids, and bases, can be volatilized at relatively low temperatures, and is imageable with a visible laser by a photothermal process. The polymer is processed without solvent, is recyclable by sublimation, and is indefinitely stable at room temperature at atmospheric pressure. PNND is 100% recyclable as there appears to be no fatigue from recycling the polymer for the CVD process.

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