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# Photopatterning of Indomethacin Thin Films: a Solvent-Free Vapor-Deposited Photoresist

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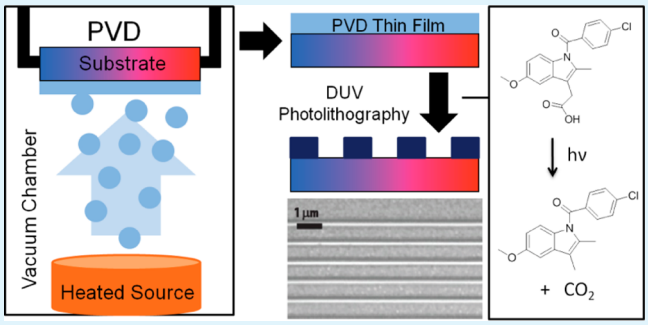
**ABSTRACT:** We report indomethacin as a photoresist that can be dry-deposited (as well as spin-coated), and developed in weak aqueous base. This is the first reported patterning of indomethacin as a resist material. Nanometer-scale patterns were achieved through DUV photolithography and the underlying patterning mechanism was investigated.




**KEYWORDS:** *indomethacin, vapor deposition, photolithography, organic glass, spin coating, dry deposition*

Photolithography is a process used to produce small-scale features that is extensively used by the semiconductor industry, mainly in the manufacture of integrated circuits. Additionally, the lithographic process is increasingly finding use in developing fields which require small scale structures such as biotechnology, organic electronics or photonics. Often the desired structures are delicate and may interact in undesirable ways with the current chemical systems used in modern photoresists. Therefore, it may be valuable to reduce or eliminate solvent exposure[1] and identify patterning systems that provide mild development conditions to extend the use of photolithography into new applications. Previous efforts to reduce or eliminate the use of organic solvents have included the investigation of greener solvents including supercritical carbon dioxide,[2−5] water,[6−8] and linear methyl siloxanes.[9] Alternately, films can be prepared without solvents by using physical vapor deposition (PVD).[10,11] PVD also offers the ability to deposit a photoresist on a curved surface, a feature of growing interest as curved displays, devices, and untraditional planar structures grow in importance. Small molecules, as opposed to polymers, offer compatibility with the PVD process.

Indomethacin is a low-molecular-weight glass-forming molecule stable at high temperatures with radiation sensitivity, making it a good candidate for a small molecule resist. As a known prescription drug molecule, indomethacin is not harmful to humans at appropriate doses.[12] Previous work has shown that indomethacin can form glassy films by PVD.[13−16] Physical vapor deposition of glass-forming small molecules, such as indomethacin, onto substrates held below their glass transition temperature can result in remarkably stable glasses with higher density and lower potential energy than the same glass formed by cooling of its liquid.[13−21]

In this investigation, we test indomethacin's behavior as a resist using both spin-coated and PVD samples. It is already well-understood and characterized as a glassy material under PVD conditions, but has never been used as a photopatternable material. Here, we show the first reported pattern formation of indomethacin using dry deposition and aqueous development. We also propose the underlying mechanism that explains the solubility switch upon exposure resulting in pattern formation.

Pattern formation of indomethacin was studied using deep ultraviolet (DUV) photolithography. Spin coated samples were first employed to find optimal exposure and development conditions. Spin coated samples can be fabricated and reproduced quickly and, therefore, can be used for fast and efficient testing of lithographic parameters. Films were spin-coated using a solution of 3 wt % IMC in 2-butanone, which was filtered using a 0.2 $\mu$m pore size filter onto a silicon wafer. Films were spun at 2000 rpm for 60 s using a 1000 rpm/s ramp rate, followed by a post apply bake at 100 °C for 60 s. The resulting films had a thickness around 130 nm. After systematically screening doses and developers, it was found that a dose of 200 mJ cm$^{-2}$ and development in a weak base solution (0.002N tetramethylammonium hydroxide) produced the best results, yielding negative tone patterns. However, there

**Received:** June 16, 2015
**Accepted:** September 25, 2015
**Published:** September 25, 2015





DOI: 10.1021/acsami.5b05361
*ACS Appl. Mater. Interfaces* 2015, 7, 23398−23401

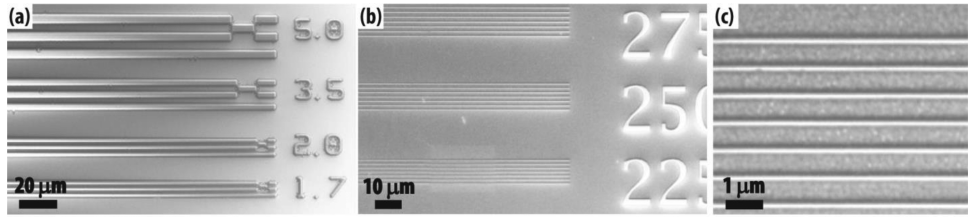



**Figure 1.** Spin coated films of indomethacin patterned by DUV photolithography showing, (a) micrometer-scale resolution, (b) nanometer resolution, and (c) a zoomed in image of 225 nm lines.

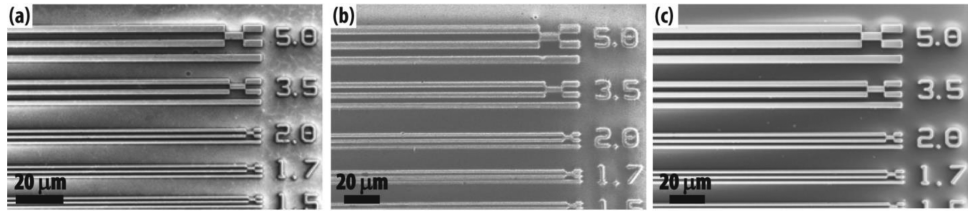



**Figure 2.** PVD samples of indomethacin patterned using DUV photolithography, obtaining micrometer-scale resolution at different substrate temperatures of (a) 245, (b) 265, and (c) 285 K.

is some residual resist remaining on the wafer after development. Using these optimized conditions, we were able to achieve high contrast patterning with micron resolution as seen in Figure 1a, using an ABM contact aligner with a 254 nm broadband wavelength light source. Additionally, we demonstrate that indomethacin has the capability of achieving nanometer resolution using an ASML DUV stepper with a 248 nm wavelength light source, as shown in panels b and c of Figure 1. Line patterns as small as 225 nm, with a 1:3 line:space ratio were obtained. These lines have a line edge roughness of 29 nm and a line width roughness of 52 nm.

To investigate the patterning behavior of PVD films, we deposited indomethacin at three different substrate temperatures, 245, 265, and 285 K. Depositing at these temperatures, which are below the $T_g$ (312 K) of indomethacin, has been shown to result in ultrastable thin films.[17] Films of indomethacin were vapor-deposited in a custom built physical vapor deposition chamber at P = $10^{-8}$ Torr. The chamber is equipped with a custom built temperature-controlled copper stage and substrate holders. Glasses were prepared by heating indomethacin (purchased from Sigma-Aldrich and used without further purification) in an alumina crucible to achieve a rate of 0.2 nm/s while the silicon wafer substrate was held at the desired temperature. Films were deposited until a final thickness of 100−120 nm was achieved. For a detailed characterization of film formation and stability using physical vapor deposition of indomethacin, the interested reader is directed to refs14, 15, and 18. Each sample was successfully patterned under the optimized conditions determined by the spin-coated samples. Photopatterning results of these PVD samples of indomethacin are shown in Figure 2. We successfully demonstrate the ability of the PVD samples to pattern micron-sized lines using DUV photolithography. Higher resolution patterns could not be obtained due to low development contrast. There was not a significant difference in the patterning behavior between the different substrate temperatures, indicating that the different packing arrangements[18] found in these three glasses do not have an effect on patterning performance for this system.

Spin-coated samples of indomethacin were able to achieve nanometer resolution, whereas PVD samples were only able to achieve micron-scale resolution, and this behavior is likely associated with the different densities of the glasses. Figure 3

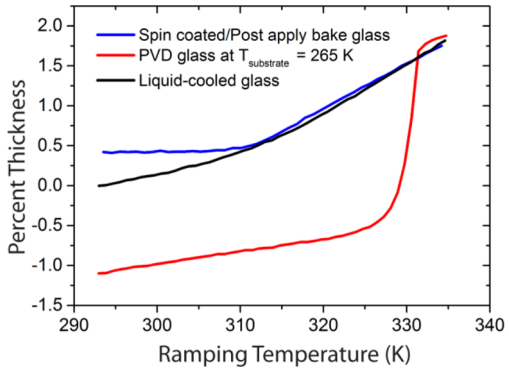



**Figure 3.** Percent thickness change of spin coated/post apply bake (blue) and PVD (red) glasses during temperature cycling, with comparison to a glass prepared by cooling the liquid at 1 K/min (black). PVD glasses are about 1% denser than an ordinary glass, whereas a spin-coated glass is 0.4% less dense.

shows that spin coated glasses are 1.4% less dense than a PVD glass deposited at 265 K. The thicknesses of a spin coated sample and a PVD sample were measured during temperature-cycling and compared with a glass cooled from the liquid at 1 K/min (ordinary glass). These measurements were performed using a J.A. Woollam M-2000U spectroscopic ellipsometer and fit with a Cauchy model (including a parameter to account for uniaxial birefringence of the PVD glass[14,18]). Before these measurements, the spin coated sample was subjected to a post apply bake treatment at 100 °C followed by rapid cooling, to emulate the procedure used to prepare samples for photolithography. PVD glasses show an onset temperature of 327 K, a result of enhanced packing in the deposited glass and previously characterized elsewhere.[14] PVD glasses deposited at 245 and 285 K are also known to be much more dense than the liquid-cooled glass. Thus, all the PVD glasses tested are considerably denser than the spin coated glass with the post apply bake. With this information, we offer two potential interpretations of the results in Figures 1 and 2. It may be that a


DOI: 10.1021/acsami.5b05361
ACS Appl. Mater. Interfaces 2015, 7, 23398−23401

less dense spin-coated glass is more susceptible to a photochemical reaction than the higher density glasses of indomethacin prepared by PVD, leading to higher resolution patterning by spin coated glasses. Alternately, the lower resolution of the PVD glass might be explained by more sluggish dissolution of the unexposed material in comparison to the spin coated glass.

It is important for potential further optimization of any new photoresist system to understand the patterning mechanism and the underlying chemical changes that cause the shift in development contrast and change in solubility. We investigated the patterning mechanism of indomethacin using infrared (IR) spectroscopy and liquid chromatography mass spectrometry (LCMS). A Mattson Instruments Galaxy 2020 FT-IR was used for Fourier transform infrared analysis (FT-IR) of exposed and unexposed films. Indomethacin films were spin coated onto double polished silicon wafers, and one was exposed to 254 nm DUV light (200 mJ $cm^{-2}$). As shown in Figure 4a, the spectra

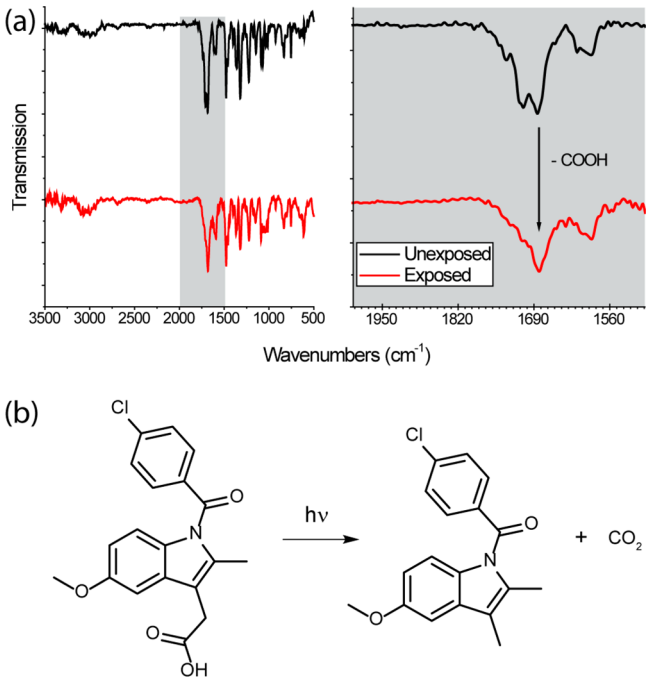



**Figure 4.** (a) FT-IR traces of indomethacin before and after exposure. A zoomed in image of the carbonyl stretching region can be seen on the right. Upon exposure, there is loss of the carboxylic acid stretching peak. (b) Proposed patterning mechanism for indomethacin using DUV lithography.

of the exposed and unexposed films are comparable except in the C═O stretching region. In the unexposed film (unmodified indomethacin) two peaks are clearly distinguishable in the carbonyl region, one representing the carbonyl of the amide group at 1685 $cm^{-1}$ and one at 1712 $cm^{-1}$ stemming from the carbonyl stretch vibration of the carboxylic acid.[22] However, in the exposed films only one peak in the carbonyl region at 1685 $cm^{-1}$ is observed. There is no peak corresponding to the carboxylic acid indicating the loss of that group upon exposure to radiation. Reverse-phase LCMS also confirmed the presence of two distinct compounds with a mass difference of 44 mass units before and after UV exposure, which corresponds to the loss of a carboxylic acid group. Therefore, it was determined that upon exposure indomethacin loses the carboxylic acid group resulting in the product seen in Figure 4b, through the release of carbon dioxide.[23,24] The loss of the carboxylic acid group allows for a solubility change between the exposed and unexposed areas in base developer. The carboxylic acid group makes the unexposed molecules soluble in base, whereas the exposed material, which lacks the carboxylic acid, is not soluble in base, allowing for negative tone patterning.

We demonstrated for the first time the use of commercially available indomethacin as a photoresist material for DUV photolithography. Thin films obtained by spin coating and PVD were investigated for comparison and showed negative tone patterning in an aqueous base developer with good pattern resolution. Spin coated samples achieved a resolution of 225 nm lines, which is roughly the limit of the exposure tool. Furthermore, we investigated the underlying patterning mechanism causing the solubility change in aqueous base. We demonstrated with IR spectroscopy and LCMS that upon DUV exposure, thin films of indomethacin lose the carboxylic acid group (in the form of $CO_2$), substantially reducing the solubility of exposed regions in aqueous base and enabling pattern formation. PVD proved to be an effective technique for deposition of indomethacin as a photoresist. Spin-coated films of indomethacin were capable of higher-resolution patterning than the PVD films, and this observation suggests that the higher density of the PVD films resulted in less effective pattern formation.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research was primarily supported by University of Wisconsin Materials Research Science and Engineering Center (DMR-1121288). This work was performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation (Grant ECCS-0335765). D.Y. was supported by KAKENHI (Grant 25708038) from the Japan Society for the Promotion of Science (JSPS).

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DOI: 10.1021/acsami.5b05361
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