

Soft Lithographic Patterning on Silicon

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In recent years, chemically modified surfaces have become increasingly important, both for their potential industrial applications, as well as scientific advances.¹⁻¹¹ Much of this interest is driven by the need to combine desired bulk properties with tailored surface chemistries. New methods for modifying surfaces allow the exploration of many potential applications, which span a wide variety of research areas. These areas, while ranging widely in their execution and ultimate goal, all bear the common interest of controlling or modifying the chemistry of the desired substrate by engineering surface properties. Areas in which modification of surface properties has proven especially useful include biology/biochemistry and materials science, the latter of which is the focus of this research.

Much work has gone into developing new methods for modifying surface properties through microcontact printing of self-assembled monolayers.^{2,7,8,11-27} Contact printing is a process in which a polymeric stamp, covered with an 'ink' appropriate for the given substrate, is brought into contact with the surface. For silicon substrates, alkyltrichlorosilane inks are used, with octadecyltrichlorosilane (OTS) the most commonly studied due to its resist properties. The structural and physical properties of contact printed OTS monolayers were fully characterized using ellipsometry, X-ray photoelectron spectroscopy (XPS), reflection-absorption infrared spectroscopy (RAIRS), atomic force microscopy (AFM), and scanning electron microscopy (SEM). These experiments demonstrated that coverages equivalent to a full monolayer were formed after 30 s of stamp contact with the substrate. The structure of the films formed was found to be densely packed, and highly oriented. While OTS was shown to have long range patterning capabilities, migration of OTS islands into underivatized regions was noted, limiting pattern fidelity and resolution. Two possible mechanisms, lateral diffusion and vapor phase transport, are thought to be responsible for these defects.

In an effort to reduce or eliminate the suspected mechanisms causing island diffusion, a less volatile alkyltrichlorosilane (docosyltrichlorosilane, DTS) was selected for the printing process. Contact printed monolayers of this new ink were fully characterized using ellipsometry, RAIRS, XPS, AFM, and SEM. These experiments found that the monolayer formation was highly influenced by the humidity present in the lab ambient conditions. At low relative humidity, a thickness equivalent to a full monolayer was achieved after 5 minutes of contact time, where as only 1 min was sufficient for the high relative humidity case. In either case, the films were found to be close packed and highly oriented. SEM and AFM studies of patterned DTS showed little spreading in the non-derivatized regions. The ability of the film to serve as a wet chemical etch resist was also studied, showing marked improvements over OTS films.

The process of contact printing was applied to two novel systems, that of orthogonal self assembly, and mixed monolayer etch resists. Orthogonal self-assembly, a process involving multiple printing steps, which uses the first printing step to serve as a patterned resist to subsequent printings. This methodology is particularly useful when applied to volatile inks that are unable to maintain pattern fidelity using traditional printing methods. In this experiment, two different inks are employed, OTS and octenyltrichlorosilane (OCT). The structures of these films were analyzed via ellipsometry, XPS, and RAIRS. OTS is shown to be close packed and highly oriented, while the modes in the OCT spectrum were too weak for

a detailed analysis. The patterning capabilities of the orthogonal self-assembly process was examined using AFM, SEM, and secondary ion mass spectroscopy (SIMS), which show the orthogonal printing process to be selective.

A methodology for controlling the nanoscale architecture of etched silicon was developed utilizing the printing of mixed monolayers. Contact printing of solutions comprised of DTS and octyltrichlorosilane (OCTY) with different mole fractions formed mixed monolayers on Si. These monolayers, depending on the concentration of DTS present in solution, showed domains of DTS surrounded by OCTY. After annealing in air, these films were placed into KOH etching solutions and the resulting grain structures were examined via AFM. The data showed that different mole fractions created different grain structures upon exposure to the etching solution. Additionally, the resulting etch structures were tested for photoluminescence, though only weak photoluminescence was noted.

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