Directed Surface Adsorption Lithography: Lithografting

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In this presentation we introduce a new and novel form of patterning based on the physical adsorption of polymers onto a flat surface. In the field of polymer thin films it is understood that polymer chains can become strongly bound to a silicon surface by physical forces, not just chemical bonds. The chains can sacrifice the entropy of their random coil configurations and form tight "loops" and long "trains" along the surface if the interaction energies are favorable. The result is a physisorbed brush-like layer that is difficult to remove, even with strong solvents.¹ We have discovered that the elevated temperatures and pressures associated with the thermal embossing form of nanoimprint lithography facilitates this surface adsorption. Films of polystyrene (PS) are spin cast from toluene onto clean silicon wafers. After spin coating, PS film can be easily removed by washing the wafer with pure toluene. However, after heating the films above the Tg of the PS and applying pressures on the order of 100 to 500 psi, the chains become strongly bound to the surface. When these films are washed in toluene, there is a thin layer of physisorbed PS that cannot be removed by the solvent. This thickness of the film can be on the order of 1 to 10 nm and depends specifically on the nature of the PS surface (hydrophilic vs hydrophobic), the molecular mass of the PS, and the temperature and pressure to which the film has been processed. As illustrated in the Figure, this surface adsorption process can be adapted into a novel form of lithography. If the thickness of the initial film is less than a critical value, incomplete mold fill will occur. In this limit the pressure from the mold is selectively applied through the tops of the pattern; pressure is not directly applied in the channels. Apparently, the polymer chains under the protrusions of the mold become selectively adsorbed to the surface. This is revealed upon washing the film with toluene. The AFM image in the Figure shows parallel lines of grafted PS between the regions of exposed silicon. This physical grafting mechanism will be discussed in detail in terms of a novel "lithografting" patterning technique. We also discuss the important role these physisorbed chains with respect to residual layer control, pattern stability, and solvent induced lift-off process.

¹ O. Guiselin, *Europhys. Lett.*, **17** (1992) 225.

"lithografting" technique



PS structures after toluene rinse



~ 800 nm pitch ~ 13.3 nm line height

