Nanopatterning technique for advanced materials

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Thermochemical nanolithography can pattern a wide range of materials by using a heated atomic force microscope tip to thermally activate chemical transformations.

Nanolithography techniques employed today have significant limitations in terms of resolution, speed, and the chemical diversity of the materials that can be patterned on an arbitrary substrate. Dip-pen nanolithography offers several interesting capabilities, but it requires stringent control over environmental atmosphere and has limitations in substrate choice, patterning speed, and change of topography. Scanning probe microscopy (SPM) technologies have become increasingly popular due to their potential application in low-cost (and now parallelized) fabrication of nanoscale structures. Recent experiments have demonstrated that SPM tips can also act as mechanical, thermal, and/or electrical sources to initiate and perform various physical and chemical processes with nanoscale resolution. Most of these techniques can theoretically create topographical nanopatterns with a spatial resolution on the order of 10nm. But achieving chemical patterning at resolutions of 100nm and below has been a challenge because of the difficulty in spatially confining reagents and because of the need to control the interactions of the reactant and products with the substrates and stamps. Recently, resistively-heated atomic force microscopy (AFM) tips have been shown to thermally activate chemical reactions at the nanometer scale at the surface of a material (see Figure 1).

In the resistively-heated AFM cantilevers, a current passes through the doped legs of a silicon cantilever to heat the tip apex. The tip’s temperature and distance from the surface can be controlled finely enough to drive heat-triggered chemical reactions with lithographic precision. We have obtained local chemical patterns at resolutions of 100nm and below has been a challenge because of the difficulty in spatially confining reagents and because of the need to control the interactions of the reactant and products with the substrates and stamps. Recently, resistively-heated atomic force microscopy (AFM) tips have been shown to thermally activate chemical reactions at the nanometer scale at the surface of a material (see Figure 1).

Figure 1. Examples of materials that can be patterned by thermochemical nanolithography (TCNL). PZT: Lead zirconate titanate. PPV: Poly(p-phenylene vinylene).

Our work demonstrated that TCNL can be used for the nanofabrication of several patterns and materials. For example, the heat treatment induces a change in the chemical functionality of acid and amine patterns on the surface of copolymers containing thermally labile groups, enabling a transformation from ester to acid groups or carbamate to amines in 80% humidity. TCNL can also create nanostructures of poly(p-phenylene vinylene), a typical electroluminescent conjugated polymer, from organic semiconductor precursors, such as poly(p-xylene tetrahydrothiophenium chloride. The result is a clear ‘turn-on’ of luminescence. We have used TCNL to build reduced graphene oxide structures through local thermal reduction of insulating graphene oxide, resulting in a 10^4 increase in conductivity for features as small as 12nm. Recently, we made arbitrary-shaped Pb(Zr0.52Ti0.48)O3 and PbTiO3 ferroelectric nanostructures through local crystallization of sol-gel derived glasses on a variety of substrates including plastic (Kapton), silicon, and soda-lime glass. TCNL can make ferroelectric lines with widths >30nm or spheres with densities up to 213Gb/in^2 and diameters >10nm.

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After the initial TCNL writing step to unmask a functional group, further functionalization or conversion of the pattern can easily be achieved. We found that an iterative application of these steps effectively increases the range of chemical groups and macromolecules that can be independently patterned on the same surface. For example, tetrahydropyranyl (THP) esters can be deprotected by TCNL to give carboxylic acids (leading to a change in the friction) when the tip temperature, scan speed, and load are appropriately chosen and controlled. For the THP ester–containing polymer, this can be accomplished at ~130°C. Upon subsequent heating above 170°C, changes in friction can also be achieved that are fully consistent with the elimination of water to form anhydrides. Thus TCNL at two different temperatures can be used, effectively, to write and erase wetting changes on a surface at the nanoscopic scale.

The technique can be applied to appropriately designed TCNL resists, such that amine patterns created on a surface by TCNL deprotection of carbamates can be converted into other functionalities (e.g., thiols) or linkers (e.g., biotin) using known coupling schemes. These post-functionalization steps can be chosen so as to not affect the untreated polymer, allowing the TCNL process to be repeated on the same surface to unmask additional amines on distinct areas of the sample. This iterative approach leads to a unique method to produce nanopatterned surfaces with multiple, orthogonal functionalities, each with their own well-defined and independent pattern. We demonstrated this in an experiment where the differently colored fluorescent areas demarcate the patterns obtained through two sequentially functionalized with different proteins and with DNA molecules. Furthermore, there are indications that the density of the functional groups on the polymer surface can be varied by patterning at different tip temperatures with a constant load.

In summary, TCNL is a very versatile technique that can produce simultaneous and partially independent chemical and topographical changes, and it can be extended to a wide range of thermally activated chemical transformations. The TCNL patterning can be performed on a variety of materials deposited on many different substrates, restricted primarily by the final application for the patterned material. In the future we hope to expand the range of chemical reactions and materials that can be patterned, and we plan to develop increasingly complex patterns, including those using chemical gradients with sub-100 nm resolution.

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References


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