Orthogonal Processing: A Novel Photolithographic Patterning Method for Organic Electronics

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Abstract:

We describe the discovery and evaluation of a semi-perfluoroalkyl resorcinarene photoresist which is processable in hydrofluoroether solvents (HFEs). This novel, high-performance imaging material is specifically designed to be orthogonal to the vast majority of organic conductors and semiconductors, and hence enable their photolithographic patterning. Furthermore, this material paves the way for the multilevel patterning of organic electronic materials, as demonstrated by the fabrication of overlaid patterns of a polyfluorene and a transition metal complex \([\text{Ru(bpy)}_3]_2(\text{PF}_6)_2\).

Summary of Research:

Organic electronics is emerging as a promising technology to enable mechanically flexible devices through solution processing of organic electronic materials [1]. As with traditional electronics, organic devices require active functional materials to be tailored into micro-patterned and multi-layered device components. While the former relies on photolithographic patterning techniques, the latter is restricted from adopting such robust, high-resolution and high-throughput techniques because of the chemical compatibility issue between organic electronic materials and patterning agents [2]. By carefully selecting less damaging processing solvents and designing new patterning materials processable in such solvents, we can enable the use of conventional lithography with sensitive organic materials.

In our search for universal, material-friendly solvents, we have identified highly fluorinated liquids (fluorous solvents), which are in general poor solvents for non-fluorinated organic materials. Among the variety of fluorous solvents, segregated hydrofluoroethers (HFEs) are attractive because of their nonflammability, zero ozone-depletion potential and low toxicity for humans [3,4]. By combining these benign solvents with specifically tailored photoresist materials, we are able to apply conventional lithography to patterning organic materials.

The next stage is to design photoresist materials which can be processed in HFEs. A design motif was hinted by molecular resists, which are amorphous small molecules with mono-disperse molecular weight distribution. Recently we have reported that a resorcinarene material possesses excellent patterning properties under conventional lithographic conditions [5]. The same molecular framework was adopted, to which four semi-perfluoroalkyl chains and eight acid-cleavable tert-butoxycarbonyl (tBoc) groups were appended. The resulting resorcinarene (Rf-Calix-tBoc) in Figure 1 is able to form a negative tone image by transformation into an insoluble form upon an
acid-catalyzed deprotection reaction, in which H⁺ is liberated from the photoacid generator (PAG) under UV exposure. Lithographic evaluation began with spin-coating films of the resorcinarene and PAG mixture on various substrates. Uniform films were cast on Si, glass and polyimide-coated wafers. Following UV exposure (84 mJ cm⁻² with Si substrate), bake (at 70°C) and development in HFE-7200, at least 600 nm features were generated on the aforementioned substrates (Figure 2). Under e-beam exposure conditions, 80 nm patterns could be achieved without extensive optimization, which demonstrates that lithography employing HFEs can be a useful tool to realize sub-100-nm features.

The new imaging material and lithographic processing in HFEs were then applied to making micron-sized patterns of organic electronic materials. Figure 3 illustrates a procedure of lift-off patterning. A developed resorcinarene image becomes soluble again in HFEs through hexamethyldisilazane (HMDS) treatment, which reprotects the phenolic hydroxyl residue with trimethylsilyl (TMS) group [6,7]. Deposition of an organic material and following lift-off of the resorcinarene film in hot HFE-7100 generate an organic material pattern. It has been demonstrated that poly(3-hexylthiophene) (P3HT), poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and Au could be patterned down to 5 µm size. As a step further, an overlaid materials pattern was fabricated to demonstrate, for the first time, the multilevel patterning of solution processable organic layers. The electroluminescent polymer poly(9,9-diocytfluorene) was patterned first according to the scheme in Figure 3, and then the same procedure was repeated with fluorescent material tris(2,2’-bipyridine)ruthenium(II) bis(hexafluorophosphate) [Ru(bpy)₃]²⁺PF₆⁻ on top of the patterned poly(9,9-diocytfluorene) film. Overlaid features down to 5 µm size were made successfully (Figure 4).

The results show that the new imaging material described here brings unique capabilities to the world of organic electronics.

Figure 2: SEM image of the developed resorcinarene on glass (scale bar is 10 µm).

Figure 3: General procedure for the lift-off patterning of functional materials.

Figure 4: Fluorescent microscope image of overlaid patterns (feature width 5 µm) of poly(9,9-diocytfluorene) (bottom) and [Ru(bpy)₃]²⁺PF₆⁻ (top).

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