Hydrogen Silsesquioxane As A Resist And Material Of Choice In Fabricating Plasmonic Antennas

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As a negative-tone electron beam resist, hydrogen silsesquioxane (HSQ) has many of the attributes of a good resist, i.e. high etch resistance, low line-edge roughness, and reliability in achieving sub-10-nm resolution in patterning. Combined with its optical properties as a low-k dielectric, and its thermal stability, HSQ can be a material of choice in plasmonic nanostructure fabrication.

Recently, we have demonstrated the use of HSQ as a dielectric spacer in metal nanodisk arrays for high-resolution color printing,¹ and in defining nanogaps between gold nanostructures through a HSQ-liftoff process.² Here, we will present two new processes involving HSQ. In the first, we propose a solution to the problem of achieving successful liftoff of HSQ without hydrofluoric acid or ultrasonic agitation in the fabrication of sub-10-nm gaps between metal nanostructures. The solution involves the patterning of HSQ as a single-use freestanding nanostencil that also allows substrates to be cleaned prior to metal deposition. By avoiding liftoff in hydrofluoric acid, which will etch silicon oxide, this new HSQ-liftoff process can be extended to silicon-oxide-based substrates and materials. Figure 1 shows a TEM of a cross-sectional slice through an array of metal nanostructures fabricated using this approach. The gaps of ~8 nm can be reliably defined across an entire array.

In the second process, we provide a means for creating high quality factor plasmonic resonators using top-down lithography. Here, the challenge is in creating structures with low density of grain boundaries, and without metallic adhesion layers, both known to cause damping of the plasmon resonances. Though annealing is a means for increasing grain sizes in polycrystalline gold inherent in lithographically-defined plasmonic structures, doing so results in a change in the shape and a tendency for the "beading up" of structures. We instead spincoat and crosslink HSQ onto the polycrystalline metal structures prior to annealing, to preserve its shape. Using this process, the quality factor of our resonators matched those of crystalline nanoparticles synthesized by chemical means, while retaining the design flexibility of top-down methods. TEM images of a structure before and after annealing are shown in Figure 2.

¹ K. Kumar, H. Duan, R.S. Hegde, S.C.W. Koh, J.N. Wei, J.K.W. Yang, *Nature Nanotechnology* 7, 557–561 (2012)

² H. Duan, H. Hu, K. Kumar, Z. Shen, J.K.W. Yang, ACS Nano 5(9), 7593-7600 (2011)



Figure 1: TEM images of cross-sectional slices through a series of gold nanostructures on a Si substrate: Gaps of ~8 nm were reliably fabricated using a process involving HSQ as a nanostencil through which gold was deposited. The trapezoidal shape of the cross section was attributed in part to the build-up of gold on the nanostencil sidewalls during deposition.



Figure 2: TEM images of a gold ring structure before (a) and after (b) annealing: By coating nanostructures with HSQ before annealing, the shape of the structures were preserved, while the density of grain boundaries within the structures decreased.