Application of hydrogen silsesquioxane (HSQ) as etching mask for dense and ultra-sharp silicon tip arrays

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Silicon tips are widely applied as field emitters and probe tips of atomic force microscope (AFM), scanning probe microscope (SPM) and related probe scanning techniques [1]. They are also used as templates for growth of carbon nanotubes [1], coating GaN, diamond nanoparticles [2] and diamond-like carbon films [3]. Therefore, ultra sharp tips with size in the order of several nanometers are increasingly demanded in those fields [4]. However, almost all the existing techniques need oxide layer as mask and extra oxidation/wet etching process for sharpening the tips [2-4]. It still remains a challenge for fabricating dense tip arrays with submicron periodicity.

Hydrogen Silsesquioxane (HSQ) consists of repeating units of H₂SiO₃ [5] and can be transformed into SiO₂-like structure after curing by either a heating process or electron beam exposure [6] as a negative tone resist with the resolution of a few nanometers. Nanoimprint on HSQ has also been reported [5] recently. In this work, we present a novel and simplified approach for the fabrication of dense and ultra-sharp Si tip arrays using HSQ as etching mask, which does not need extra oxidation/wet etching process for sharpening the tips. Firstly, a 180 nm HSO layer, Fox24 supplied by Dow Corning Ltd, is spin-coated onto a Si wafer at the speed of 9000 rpm for 1 min. Then it is written by a high-resolution vector beam writer (VB6 HR) after bake on a 150 °C hotplate for 2 min. Several patterns with different periodicities and dot sizes are written to show the validity of this approach. The periodicities are 500, 400 and 200 nm, respectively, and the dot sizes are 250, 200 and 100 nm, respectively. The exposed resist is then developed in trimethylamine (TMA) 238WA for 1 min at 50 °C. The reactive ion etch (RIE) is carried out using System90 (delivered by Oxford Plasma Technology) in fluorine based plasma. Careful processing study is carried out for optimizing the etching process with the processing parameters of etching time, etch spices, rf power, chamber pressure and gas flow rate. Finally, the HSQ masks are readily removed by a simple wet etch in buffered HF. Fig.1, Fig.2 and 3 present the SEM images of Si tip arrays fabricated with periodicity of 500, 400 and 200 nm, respectively. The tip size achieved is as sharp as several nanometers without the necessity of extra sharpening process with oxidation/wet etch treatments. Moreover, our progress is not only in replacing the SiO₂ by a simple HSQ layer. Our conclusion is, using this novel technique with HSQ as an etching mask, we have successfully achieved high density tip arrays (200 nm pitch) thanks to the high resolution nature of HSQ in EBL and earlier work on hot developing. The density is increased by a factor of 2500 comparing to the reported in reference [3] and 40 as in reference [2]. Since the distance between tips is very close to their emitting wavelength, it

may offer a unique opportunity for scientists to study new emission characteristics with closely spaced Si tips, which is still under our study.

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Fig.1 SEM image of Si tip array with periodicity of 500 nm. Inset is the image before etching away the residual HSQ masks.



Fig.2 SEM image of Si tip array with periodicity of 400 nm.



Fig.3 SEM image of Si tip array with periodicity of 200 nm.