Direct patterning of plasma enhanced chemical deposition silicon dioxide by electron beam lithography

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Hydrogen silsesquioxane (HSQ) is a popular high resolution negative tone resist for electron beam lithography.[1,2,3] This work investigates whether an HSQ-like film can be mimicked via plasma enhanced chemical vapor deposition (PECVD) rather than spin coating. There are a number of reasons for investigating such an approach, including being able to deposit on non-planar surfaces not easily coated by spin coating.

Direct pattering of silicon dioxide films appears to have first been investigated by O'Keeffe and Handy.[4] Electron exposure, using 1-15 keV acceleration voltages, of thermally grown silicon dioxide films was found to have a three times faster etch rate in a hydrofluoric based etch than unexposed regions. The sensitivity was quite low at $1C/cm^2$. Later work investigated a sacrificial layer of PMMA on top of thermal oxide to remove beam contamination which interfered with the oxide etch[5]. Also, the use of carboxylic acids was researched to enhance the etch rates of electron exposed thermal oxide using high temperature HF vapor etching.[6]

To this author's knowledge, no investigation has been reported on electron exposure of PECVD silicon dioxide. PECVD silicon dioxide typically uses SiH_4 and N_2O gases in an RF parallel plate reactor under vacuum. It has been reported that the SiH_4 / N_2O flow ratio, pressure, and temperature affect the relative amount of hydrogen, oxygen and silicon contained in the silicon dioxide, the index of refraction, wet etch rate, density, and stress, among other parameters.[7,8,9,10] Results consistent with prior publications are obtained. For instance, an increase in the SiH_4 / N_2O flow ratio increases the index of refraction (Fig. 1) and the relative Si-H concentration (Fig 2.)

New information presented by this paper includes the results of electron exposure at 100kV accelerating voltage and subsequent development in a 1 minute buffered oxide etch (BOE) immersion (Fig 3). In this case, the oxide displays a negative tone behavior unlike thermal oxide which showed a positive behavior. The sensitivity is observed to increase with decreasing SiH_4 / N_2O ratio and therefore is more resistant to the BOE etchant. Interestingly, at weak exposure doses it observed that the film displays a positive tone behavior. These results are to be discussed in further detail. Unfortunately, the PECVD oxide has a low sensitivity ($> 1C/cm^2$) and very low contrast which may limit its practical application, if any, to grayscale lithography.

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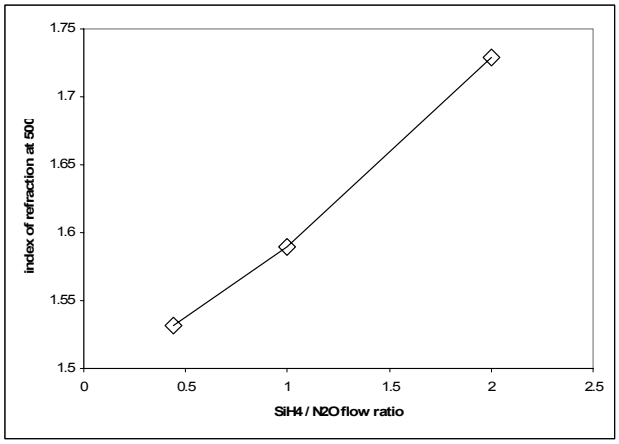

Figure 1: Index of refraction measured at 500nm versus SiH_4 / N_2O flow ratio

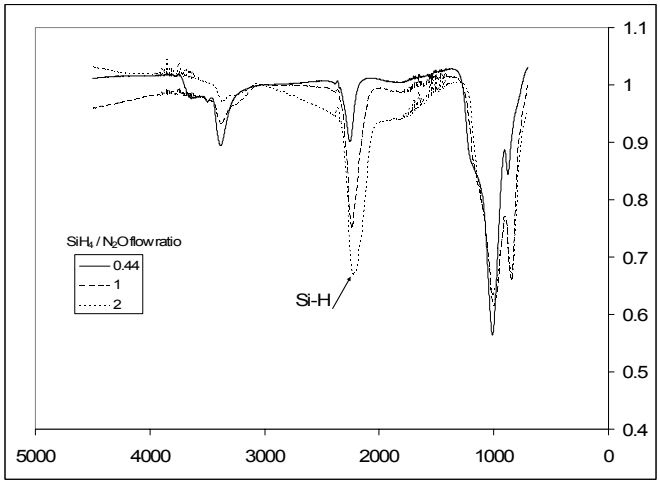

Figure 2: FTIR measurements with relative Si-H concentration at $2250cm^{-1}$

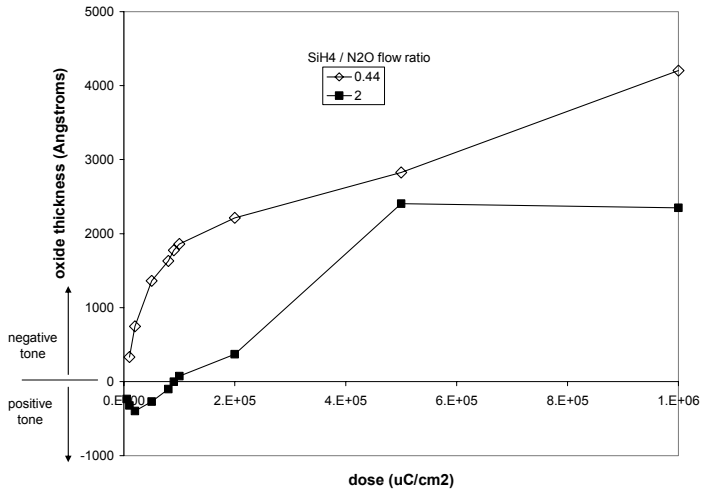

Figure 3: Resist thickness measurements of exposed regions relative to unexposed regions post BOE develop.