Controlling the adhesion of nanoscale hydrogen silsesquioxane patterns

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Hydrogen silsesquioxane[2] (HSQ) has become the electron beam lithography (EBL) resist of choice for negative tone nanoscale patterning primarily due to its high resolution. HSQ/polymer bilayers were reported[3,4] to extend the etch budget of thin HSQ. In a previous work[4], the adhesion of HSQ to a polymer used in a bilayer scheme was observed to be a function of post lithographic critical dimension (CD). In this work we propose a mechanism for the adhesion of HSQ to polymer underlayers. We also demonstrate a plasma-based surface treatment technique for controlling the adhesion of HSQ patterns to underlying materials.

The generally accepted crosslinking reaction for HSQ was presented by Namatsu, et al[2] (Fig. 1-a). Based on this model, we hypothesized that adhesion of nanoscale HSQ patterns can be strongly influenced by the presence of a bound OH group at the polymer surface (Fig 1-b). To test this hypothesis we explored two polymer systems: a polyhydroxystyrene (PHOST)-based planarizing layer known to have high OH content and an anthracene-based anti reflective coating (ARC) known to have minimal OH content. Adhesion was measured empirically by observing pattern yield as a function of CD. Exposure results and process details are shown in Fig 2. Nanoscale patterns formed on PHOST showed significantly better adhesion compared to ARC. This result agrees well with the proposed role of OH groups in determining HSQ adhesion.

To control HSQ adhesion independent of underlayer material chemistry we explored the use of plasma-based processing prior to HSQ coating. We found that ARC exposed to a 10 sec H_2 plasma showed superior adhesion at CD = 11 compared to PHOST. The plasma exposure leaves H radicals on the specimen surface which can react with ambient conditions to create OH groups prior to HSQ coating. In contrast, ARC exposed to fluorocarbon (FC) plasma eliminated all OH groups from the surface resulting in poor adhesion independent of CD. Increased H_2 plasma exposure to 30 sec yielded lines at CD = 9 nm (Fig. 3). These results are consistent with water contact angle data obtained for HSQ, PHOST and ARC (Fig. 4). A detailed characterization of these processes and their application to improving HSQ adhesion on other materials will also be presented.

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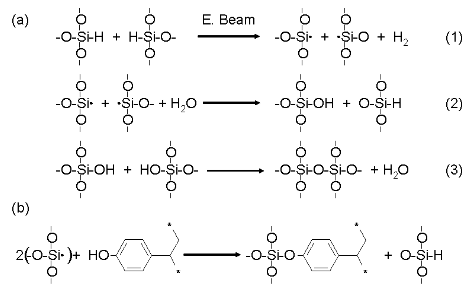

Fig 1: (a) Crosslinking mechanism of HSQ based on Ref. 2. In brief, EBL exposure of HSQ results in the formation of a network-like structure through the scission of Si-H bonds. Siloxane bonds are then formed through a reaction with H_2O and unstable silanols. (b) Proposed adhesion mechanism of HSQ to polymer surfaces based on equation 2. The presence of a bound OH group enables covalent attachement of the HSQ to the polymer surface.

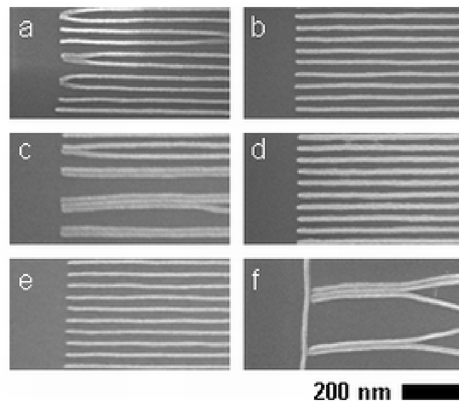

Fig 2: Scanning electron microscope (SEM) images of adhesion test patterns consisting of 5 nm wide 1 µm long lines at a 40 nm pitch. Line ends are shown to emphasize adhesion (a) NFC, CD = 11 nm, 12.5 mC/cm^2 dose. (b) NFC CD = 13 nm, 14 mC/cm^2 dose. (c) ARC, CD = 11 nm, 12.5 mC/cm^2 dose. (d) ARC, CD = 19 nm, 17 mC/cm^2 dose. (e) ARC + H_2 plasma, CD = 11 nm, 12.5 mC/cm^2 dose. (f) ARC + FC plasma, CD = 13 nm, 14 mC/cm^2 dose. All exposures were performed using a Vistec VB6 – HR EWF operated at 100 keV with a 10 nA beam current and a 5 nm pixel size. 20 nm thin HSQ was spun directly onto the underlayers and exposed without performing a post application bake. Patterns were developed using a 0.26*N* solution of tetramehtyl ammonium hydroxide (TMAH) for 4 minutes. A post exposure bake was not used in this work.

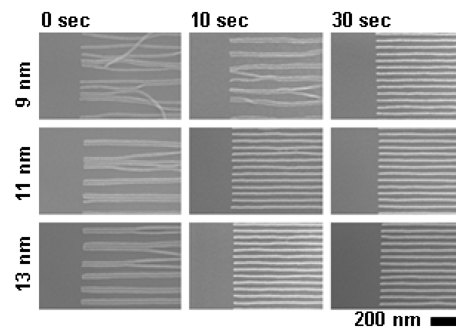

Fig 3: SEM images of HSQ patterns on ARC with 0, 10 and 30 sec of H_2 plasma exposure for CD = 9, 11 and 13 nm. Exposure conditions were identical to the ones described in Fig. 2 where CD = 9 nm corresponds to a dose of 11 mC/cm^2.

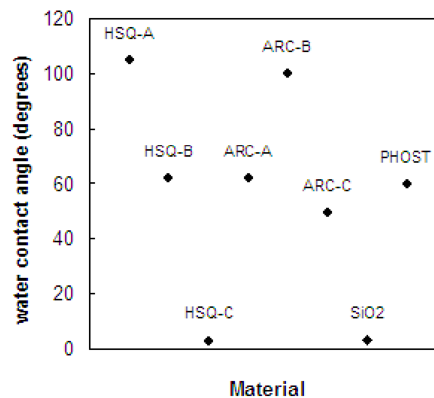

Fig 3: Contact angle of water as a function of substrate surface and surface treatment. HSQ-A: as coated, unbaked HSQ; HSQ-B: same as HSQ-A followed by 175 °C/1 min bake; HSQ-C: same as HSQ-A followed by an electron beam cure with a dose of 1000 uC/cm^2 @ 10 keV using a flood gun followed by develop using 0.26*N* TMAH for 4 min; ARC-A: as coated with 225 °C/1 min bake; ARC-B: same as ARC-A followed by FC plasma treatment; ARC-C: same as ARC-A followed by H_2 plasma/10 sec; SiO_2: Si with native SiO_2; PHOST: as coated with 175 °C/2 min bake. HSQ-B has a contact angle close to ARC-A and PHOST. However, HSQ-C more closely simulates exposed HSQ patterns and has a contact angle similar to SiO_2. ARC-C has the lowest contact angle of the polymer surfaces, providing a more favorable surface energy for patterned HSQ adhesion.