Hydrogen silsesquioxane for direct electron-beam patterning of step and flash imprint lithography templates

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The feasibility of using hydrogen silsesquioxane (HSQ) to directly pattern the relief layer of step and flash imprint lithography (SFIL) templates has been successfully demonstrated. HSQ is a spin-coatable oxide, which is capable of high resolution electron-beam lithography. Negative acting and nonchemically amplified, HSQ has moderate electron-beam sensitivity and excellent processing latitude. In this novel approach, $6 \times 6 \times 0.25$ in.^{3} quartz photomask substrates are coated with a 60 nm indium tin oxide (ITO) charge dissipation layer and directly electron-beam written using a 100 nm film of HSQ. Direct patterning of an oxide relief layer eliminates the problems of critical dimension control associated with both chromium and oxide etches, both required processes of previous template fabrication schemes. Resolution of isolated and semidense lines of 30 nm has been demonstrated on imprinted wafers using this type of template. During this evaluation, a failure of the release layer to provide a durable nonstick surface on ITO was discovered and investigated. This problem was successfully remedied by depositing a 5 nm oxide layer over the patterned ITO/HSQ template. [DOI: 10.1116/1.1515311]

I. INTRODUCTION

Step and flash imprint lithography (SFIL) is being developed as a possible low cost alternative next generation lithography (NGL).[1,2] Unlike conventional optical methods that use a mask to project an aerial image onto a wafer substrate, SFIL replicates patterns by using a template having a relief image etched into its surface. To form a pattern, an organosilicon, photocurable liquid is placed onto a wafer, and the template relief surface is pressed into contact with the substrate using minimal pressure. A broadband illumination source is used to flood expose the imprint area through the back of the transparent template. This cross-links the photocurable material and forms a polymer replica of the template relief. It is largely the absence of any image projection optics and the simplicity of the irradiating source that make SFIL a low-cost process. In spite of its relative simplicity and low cost, SFIL has demonstrated resolution below 30 nm.[3]

Templates have typically been fabricated from chromium-coated photomask blanks using standard phase shift etch processing techniques,[1] and more recently with very thin chromium to decrease etch bias and improve resolution.[3,4] Both processes result in a transparent, all-quartz template with an electron-beam (e-beam) patterned relief image etched into its surface.

In still another approach, a 6025 quartz mask blank is coated with a thin transparent conducting oxide (TCO) film such as indium tin oxide (ITO), followed by coating with a thin layer of SiO_2 deposited using chemical vapor deposition (CVD).[5] The substrate is then coated with resist and e-beam patterned. Finally, using the resist as a mask, the oxide is etched to provide the template's relief surface. This methodology offers several advantages over the chromium/quartz fabrication scheme. The significant critical dimension (CD) bias associated with etching chromium is eliminated. Incorporation of a transparent ITO layer as a permanent element into the template provides charge dissipation for both e-beam writing and subsequent scanning electron microscopy (SEM)-based inspections.[6] The ITO layer also adds contrast to an all-quartz template necessary for optical inspections. Finally, the ITO layer acts as an etch stop during the oxide etch, mitigating loading effects which would otherwise cause an etch depth bias between small and large features. Using this methodology, Dauksher *et al.*[6] have demonstrated imprinted features as small as 20 nm.

The current work involves using hydrogen silsesquioxane (HSQ; FoX-12, Dow Corning) as a spin-coatable organic silicon oxide which is directly e-beam written. While the primary use of HSQ is as a low-*k* dielectric, several investigators have demonstrated its usefulness as a high-resolution e-beam resist. Resolution of sub-20 nm features has been shown.[7–9] In its cured state, HSQ becomes a durable oxide making it a very convenient material for direct patterning of SFIL template relief structures. Processing of HSQ as an e-beam resist is less complicated since it is not chemically amplified and can be developed in the standard tetramethyl ammoniumhydroxide (TMAH) based developers used commonly for conventional resists. In addition, HSQ is especially well-suited for patterning on thick and insulating substrates such as 6025 plates. A wide process latitude and relative invariance to changes in softbake conditions make for robust processing and consistent results. Direct patterning of SFIL relief structures would also provide improved CD

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control through elimination of the oxide and/or chromium etches associated with previous fabrication methods, while saving several processing steps.

In this study, characterization and analysis of the quality and feasibility of SFIL template relief structures made with HSQ is presented. This analysis includes atomic force microscopy (AFM) of template surfaces for both ITO field and exposed HSQ regions. The linearity, exposure latitude, and contrast of HSQ used as a direct-write material on ITO is also examined. Finally, SEM images of features from both templates and imprinted wafers are shown. Additional design considerations such as the compatibility of the fluoroalkylsilane release layer with ITO and HSQ are also discussed.

II. EXPERIMENT

Templates were fabricated on $6 \times 6 \times 0.25$ in.^{3} (6025) quartz mask blanks supplied by Ulcoat. ITO films were deposited in a customized rf sputter system operating at a power of 100 W and an Ar/O_2 pressure of 6 mTorr. The films were then annealed at 350 °C for 10 min on a hotplate to further increase conductivity and optical transmission at 365 nm. Plasma enhanced chemical vapor deposition (PECVD) oxide was deposited in a Plasma Therm 790 system at a temperature of 250 °C.

A Leica VB6 electron beam exposure system operating at 100 keV with a thermal field emitter source was used for all exposures. Resolution patterns were exposed using a pixel size of 5 nm, with a beam current of 1 nA and a spot size of 7 nm. HSQ was supplied by Dow Corning as FoX-12 or FoX-15, and was diluted using methyl ethyl ketone (MEK) as needed to achieve the desired film thickness of 80–100 nm. Coating of 6025 plates was done on a Laurell spinner system with softbaking performed on a Cee® model 100 hotplate. Development of exposed substrates was done using Shipley LDD26W developer.

AFM images were collected in ambient using a Digital Instruments Dimension 3000-1 system in tapping force mode. Film thickness measurements were performed on a Nanometrics model 210XP and a Tencor Instruments Alpha Step 300 profilometer. SEM and critical dimension results were obtained using Hitachi 7800 and Hitachi S4500 field emission CD SEMs.

The x-ray photoelectron spectroscopy (XPS) data were obtained using a Physical Electronics PHI5700 ESCA system equipped with an Al monochromatic source (Al $K\alpha$ radiation at 1486.6 eV). Wide range (survey) scans were obtained with a step size of 1 eV and pass energy of 93.9 eV; high resolution scans were taken with a step size of 0.1 eV and pass energy of 11.75 eV. The Ag $3d_{5/2}$ XPS peak at 368.3 eV from a sputter-cleaned Ag foil was used to calibrate the system.

Following pattern fabrication, a 1×1 in.^{2} square imprinting template containing the relief image was cut from the center region of the 6025 plate using a precision diamond wheel saw. The template was cleaned using a Jelight UVO-42 UV-ozone cleaner, and then vapor primed with a low surface energy release agent monomer (Gelest tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane) and annealed. The template was mounted in the SFIL imprint stepper located at the Texas Materials Institute, University of Texas at Austin, where it was used to print 200 mm wafers. Prior to printing, wafers were coated with a 60 nm transfer layer consisting of Shipley AR2 600 DUV antireflective coating. The photocurable material used to replicate the relief pattern on the wafer consisted of 4 wt. % Darocur 1173 (Ciba) photoinitiator in 1,3-bis(methacryloxypropyl)tetramethyldisiloxane.

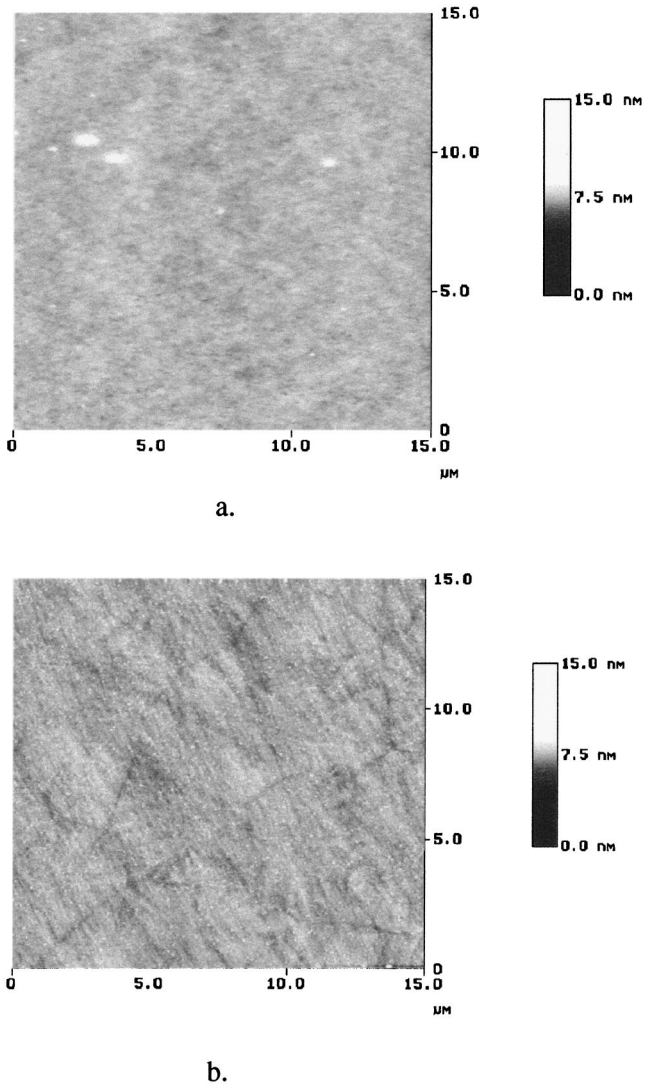
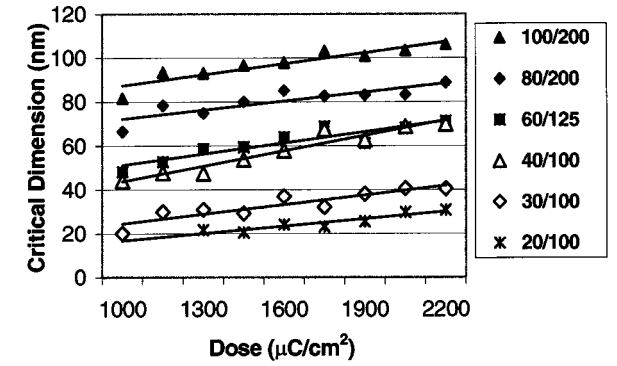


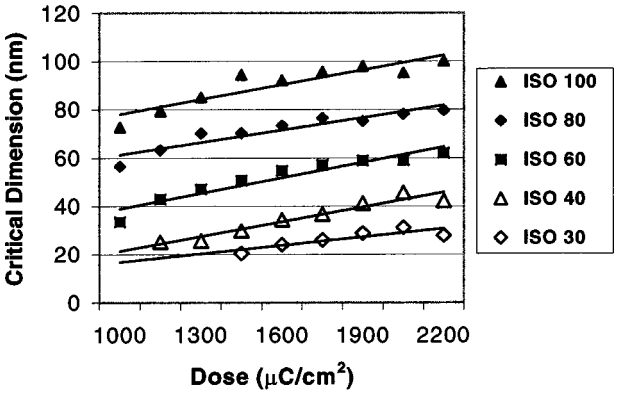
FIG. 1. AFM of an e-beam exposed region of a HSQ surface (a), and AFM of surface of a CVD SiO_2 on ITO (b).

III. RESULTS AND DISCUSSION

AFM analysis of an exposed region of HSQ after developing is shown in Fig. 1(a). The peak to valley range over a 15 μm per side square area was 16.2 nm; the corresponding rms roughness is approximately 0.26 nm. These values suggest that while the surface is generally very smooth, some spikes or undulations are present which affect surface contour. For comparison, AFM analysis [Fig. 1(b)] of an ITO



a.



b.

FIG. 2. Exposure latitude of HSQ for semidense lines expressed as line size (nm)/space size (nm) (a), and exposure latitude of HSQ for isolated lines (b).

surface covered with 15 nm of PECVD oxide taken over a 15 μm square area shows a peak to valley range of 17.6 nm and a rms roughness value of 0.51 nm.

Critical dimension measurements of resolution pattern features were recorded for a dose array ranging from 1000 to 2200 μC/cm^2. The results of these measurements are shown in Fig. 2(a) for semidense lines and in Fig. 2(b) for isolated lines. HSQ shows good CD linearity of lines from 20 to 100 nm in size as well as excellent exposure latitude over this dose range. The operating dose that could be expected to produce semidense lines to size was approximately 1400 μC/cm^2, while that for isolated lines was approximately 1900 μC/cm^2.

Analysis of HSQ contrast on an ITO-coated quartz wafer was done by measuring retained film thickness of exposed 100 μm square regions over a dose range of 100–1000 μC/cm^2. From this data the contrast, γ, was calculated to be 1.63, a value that is in close agreement with previously reported results.[8] A material with this moderate level of contrast would be expected to produce scumming and bridging of unexposed regions between dense lines. This artifact was generally observed to a varying degree for dense lines exposed at higher doses and/or where spacing was equal to or less than the HSQ thickness of 90 nm. While scumming in conventional resists is objectionable since it often causes poor etch pattern transfer, SFIL processing may be more forgiving as long as the thickness of scumming is not significant.

Figure 3 depicts top down SEM images of the finished template for a variety of line sizes and pitches at e-beam doses of 1150 and 1900 μC/cm^2. Line edge roughness is

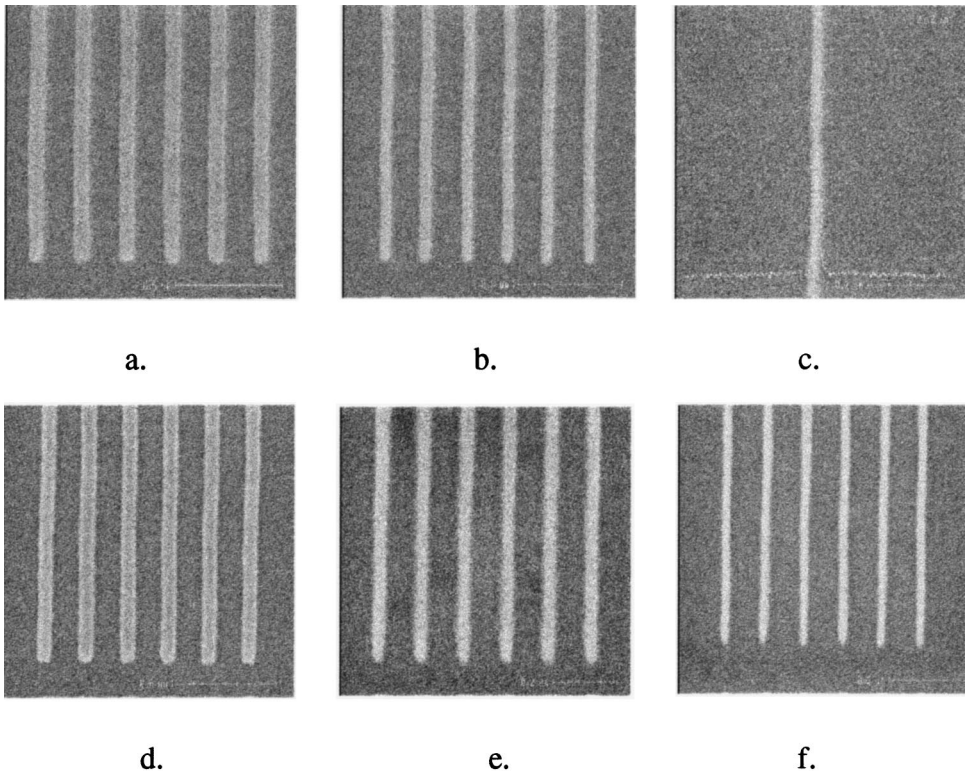


FIG. 3. Top down SEM micrographs of a HSQ/ITO template expressed as designed line CD/designed space CD, e-beam dose; actual measurement: (a) 80/125, 1150 μC/cm^2; 78 nm, (b) 60/125, 1150 μC/cm^2; 52.8 nm, (c) 40 nm iso, 1150 μC/cm^2; 25.2 nm, (d) 60/125, 1900 μC/cm^2; 61.2 nm, (e) 30/100, 1900 μC/cm^2; 38.1 nm, and (f) 20/100, 1900 μC/cm^2; 25.5 nm.

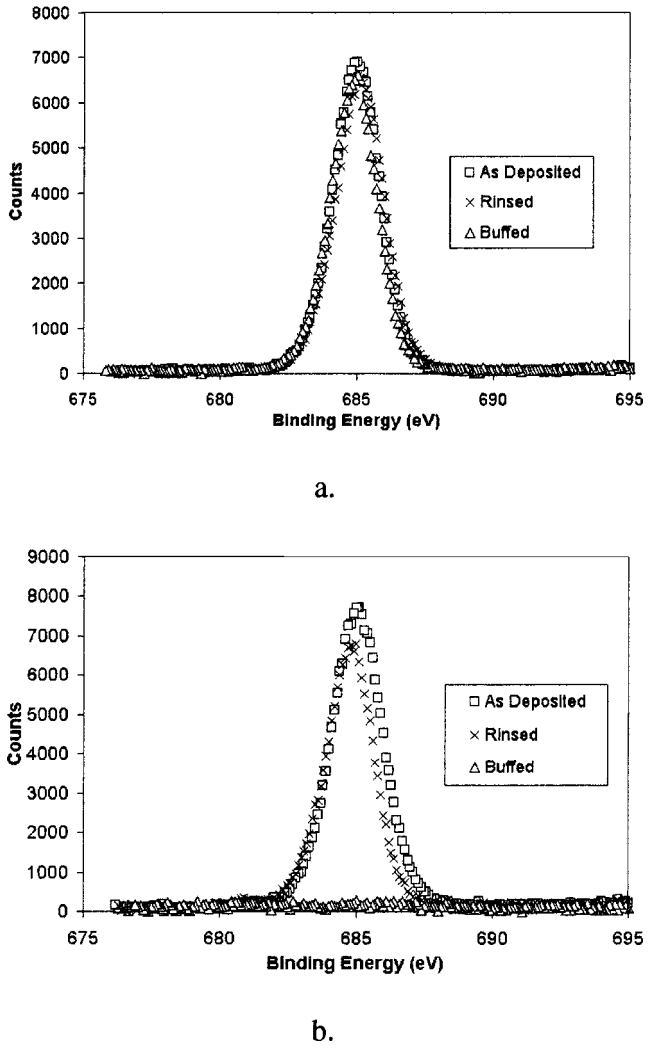


FIG. 4. F 1*s* XPS spectra of a quartz/ITO/oxide sample with SiO_2 surface (a) and quartz/ITO sample with ITO surface (b), illustrating the lack of durability of the fluorocarbon release layer on the ITO surface.

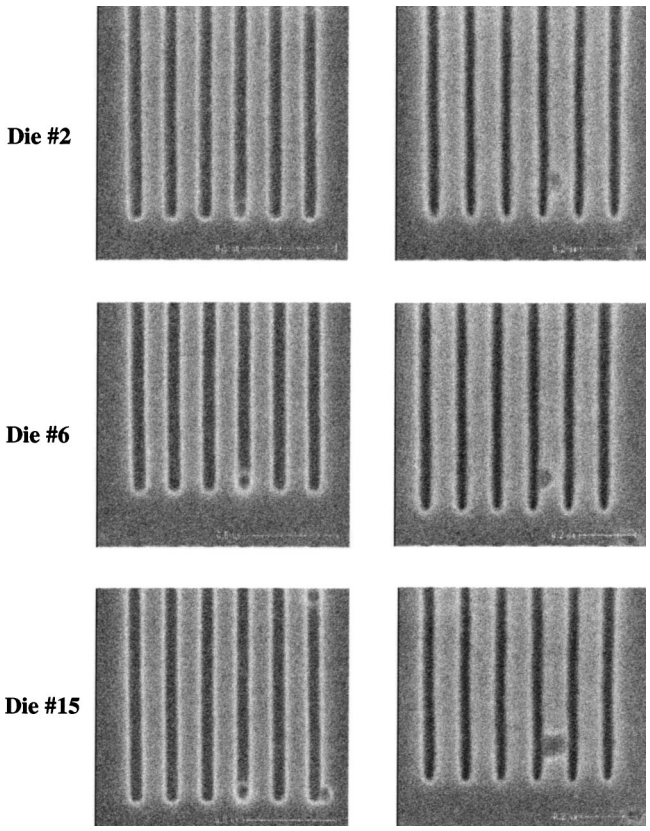


FIG. 5. SEM micrographs of top down die-to-die comparison of 60 nm/125 nm and 30 nm/100 nm semidense lines for three different die on the same wafer.

minimal and resolution is excellent with no scumming or bridging evident. Figure 3(e) depicts 30 nm/100 nm semidense lines with a trace level of scumming evident.

The first imprinting tests done using an ITO/HSQ template resulted in complete delamination of the cured etch barrier from the wafer, with the etch barrier remaining adherent to the template surface. Since the printing surface of the template is comprised of over 95% ITO, the failure of the release layer was especially catastrophic. Use of the fluoroalkylsilane release agent, while successful for quartz templates,[10] had never been studied for use with ITO surfaces. Therefore the failure of this test, though disappointing, was not entirely unexpected. Dauksher *et al.*[6] used temperature programmed desorption of methanol to compare the surfaces of SiO_2 and ITO. Their results indicate the surface hydroxyl groups on ITO bond methanol less strongly than those on SiO_2, which may indicate a difference in hydroxyl group reactivity. In order to further investigate this phenomenon, samples with SiO_2 and ITO surfaces were treated with the release agent, annealed, and subjected to various treatments. The samples were rinsed in acetone and isopropyl alcohol (IPA), and then buffed with a cleanroom wipe saturated with IPA to simulate the mechanical effects possibly seen during imprinting. XPS analysis of the F 1*s* signal from the surfaces indicates that the fluorocarbon layer bonded to the SiO_2 surface remains intact after ultrasonic bath treatments in the solvents, and also remains after the light buffing. The film on the ITO, however, is present after the solvent bath, but is almost completely removed during the buffing step. These data are shown in Fig. 4.

In an attempt to remedy this, the next template was capped with a 5 nm layer of CVD SiO_2, coating both the ITO and patterned HSQ surfaces. Since the silane based release layer has been shown to adhere strongly to quartz through reactions with silanol functional groups,[9] surface modification of ITO by addition of an oxide layer would be expected to provide a more compatible surface chemistry.

Figure 5 shows top down SEM micrographs of an imprinted wafer taken from three different die (imprint Nos. 2, 6, and 15) corresponding to the same template site, featuring 60 nm/125 nm and 30 nm/100 nm semidense lines. Resolution of these images is again excellent, in replication of the template. Repeating defects are evident, however, in both 60/125 and 30/100 line sets, with individual defects from both sets observed to be progressively worsening. Previous work has shown that SFIL templates pretreated with a fluoroalkylsilane release layer exhibit a self-cleaning mechanism

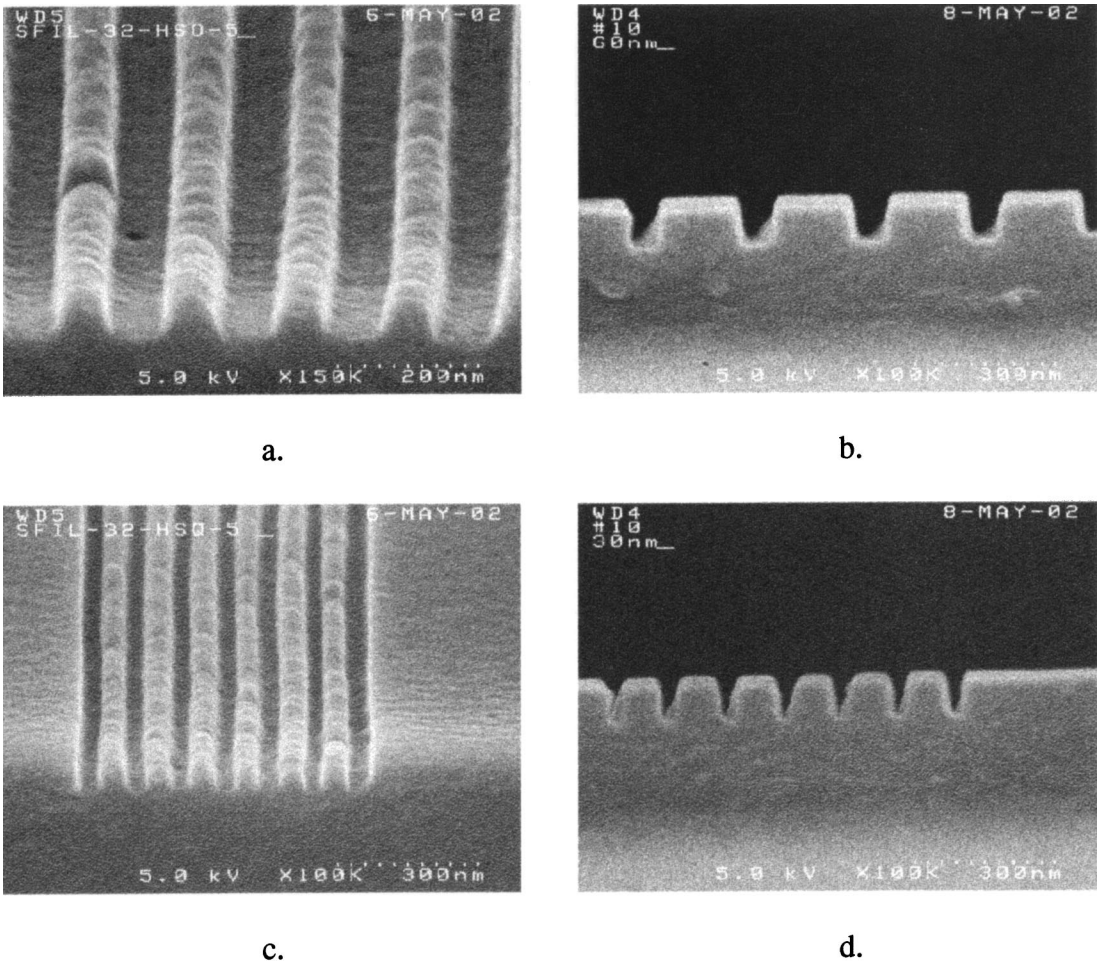


FIG. 6. Cross-sectional SEMs of imprinted wafer (a) 60 nm 1:1 pitch, (b) 60 nm 1:5 pitch, (c) 30 nm 1:2 pitch, and (d) 30 nm 1:3 pitch.

whereby defects deposited on the template after pretreatment are removed during the printing process via contact with the etch barrier.[10] As a result of this tendency, a template can rid itself of defects by printing more die. The nature and cause of the template defects that led to the printed defects shown in the progression of Fig. 5 is not known. However, it appears from this series of micrographs that once a template defect is established, a nucleus for continued growth might also be created.

Angled and cross sectional SEM photos depicting 30 and 60 nm dense and semidense lines of an imprinted wafer are shown in Fig. 6. While these images show a high level of

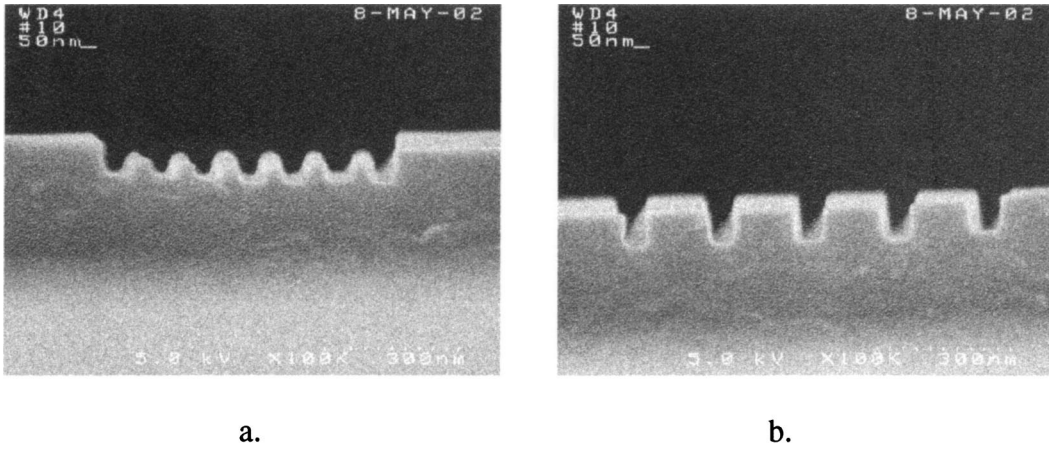


FIG. 7. SEM cross-section micrographs of an imprinted wafer illustrating 50 nm lines and the effect of HSQ scumming of dense features (a) 1:1 pitch and (b) 1:3 pitch.

resolution, excessive roughness and rounding is noted at the tops of features. This condition is worse for lines having a narrower pitch. This result is not surprising given the high degree of scumming between lines noted on the template. Figure 7(a) further illustrates this phenomena showing rounded and shallow imprinting of 50 nm lines having a 1:1 pitch; the result of a highly scummed dense line region. In contrast, Fig. 7(b) shows imprinted 50 nm lines having a 1:3 pitch with well-defined sidewalls and a full aspect ratio.

IV. CONCLUSIONS

Direct e-beam patterning of HSQ has been used successfully on 6025 quartz/ITO substrates to fabricate the relief layer of SFIL templates. Resolution of 20 nm on templates and 30 nm on imprinted wafers was achieved. AFM analysis showed that surface roughness of ITO and HSQ is very low and well within limits useful for SFIL. e-beam patterning of HSQ on 6025 plates demonstrated that HSQ offers very good latitude and linearity, but possesses only moderate contrast that results in scumming between dense features especially at high doses. The fluoroalkylsilane release layer, used previously for quartz SFIL templates, failed on bare ITO surfaces allowing the photocurable etch layer to stick to the template. This problem was overcome by depositing a 5 nm oxide layer over the patterned ITO/HSQ template.

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