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Sub-20 nm laser ablation for lithographic dry development

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Abstract
Pattern collapse of small or high aspect ratio lines during traditional wet development is a major challenge for miniaturization in nanolithography. Here we report on a new dry process which combines high resolution resist exposure with selective laser ablation to achieve high resolution with high aspect ratios. Using a low power 532 nm laser, we dry develop a normally negative tone methyl acetoxy calix(6)arene in positive tone to reveal sub-20 nm half-pitch features in a ∼100 nm film at aspect ratios unattainable with conventional development with ablation time of 1–2 s per laser pixel (∼600 nm diameter spot). We also demonstrate superior negative tone wet development by combining electron beam exposure with subsequent laser exposure at a non-ablative threshold that requires far less electron beam exposure doses than traditional wet development.

S Online supplementary data available from stacks.iop.org/Nano/23/185301/mmedia

(Some figures may appear in colour only in the online journal)

The continuous shrinkage of electronic, mechanical, and optical devices creates lithographic challenges that require non-conventional solutions. One major challenge for radiation-based lithographies (e.g. using 193 nm immersion, interference, electron beams, extreme ultraviolet, ion beams) is the pattern collapse of resist features. Tanaka *et al* showed that capillary forces during the drying of developed patterns cause collapse, as indicated by line bending, breaking, and loss of adhesion [1]. Since this initial finding, pattern collapse has been noted as one of the critical hurdles for reaching 16 nm nodes and beyond in microelectronics [2]. Researchers have tried to reduce pattern collapse via surfactants [3–6], surface modifiers [7], alternative drying solvents [8], modulus increase [9] and mechanical supports [10]. Those solutions have only modest effects because pattern collapse is predominantly a feature aspect ratio dependent phenomenon [1]. Capillary free drying processes such as ones based on supercritical CO_2 [11] and freeze-dried tert-butyl alcohol [12] can be more impactful but suffer from low throughput and deleterious water contamination. To overcome pattern collapse and thereby move further towards miniaturization, here we present a novel laser-based dry development technique which selectively ablates the exposed resist, revealing patterns up to sub-20 nm half-pitch with aspect ratios greater than 5:1.

Dry development of resists goes back to as early as 1973 [13]. The process is deemed dry because the resist is directly volatilized and the relief pattern is developed either during the exposure process (self-developing) [14, 15, 13], or during subsequent processing steps such as baking for thermal desorption [16]. There have been several examples using chemically amplified resists [17, 18]. The use of lasers for controlled ablation of organic matter was first observed in 1982 [19, 20] and has been extensively used in polymer processing and manufacturing [21, 22]. For lithography, laser ablation has been used for direct-write of polymers with resolution approaching the diffraction limit. The vast majority of such applications employ UV radiation for two reasons:

[3] Equal contributions.

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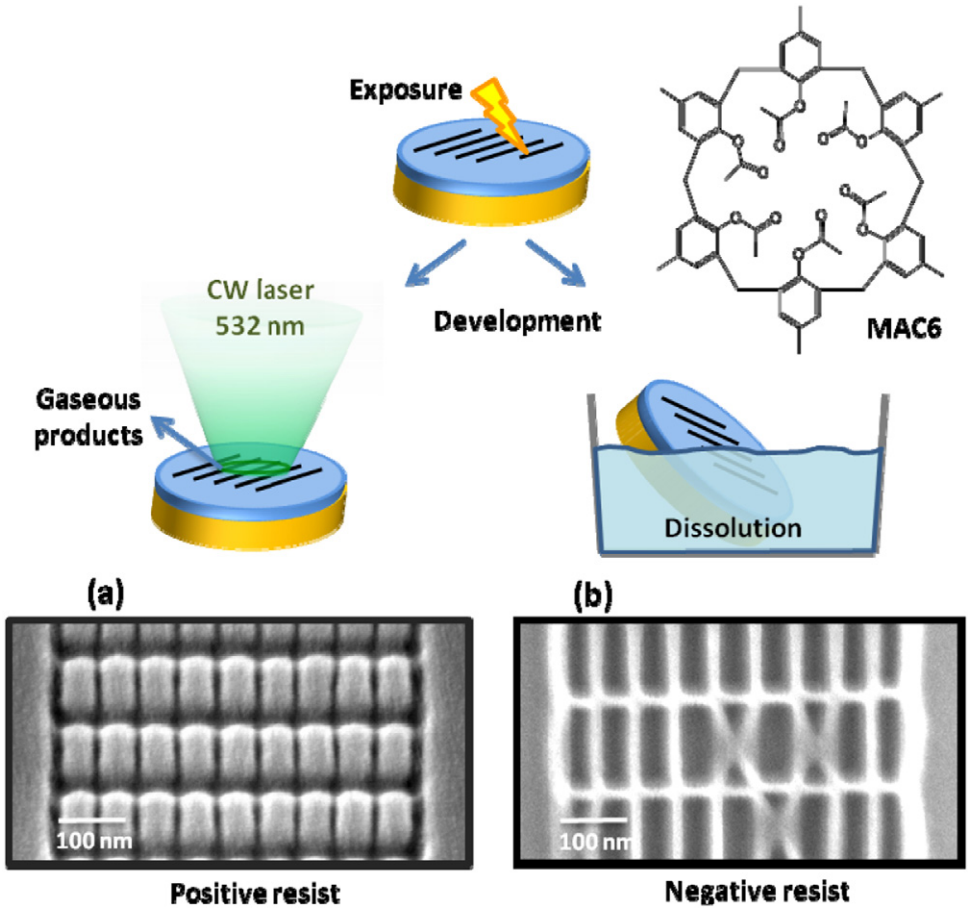

Figure 1. Comparison of laser dry development and standard wet development for the resist methyl acetoxy calix(6)arene (MAC6). The spin coated MAC6 film is electron beam exposed and then undergoes development. (a) Dry development using a 532 nm CW laser to volatilize the e-beam exposed MAC6 in positive tone. In the SEM image (45° tilt), 11 nm trenches are shown for 60 nm pitch lines. (b) Standard wet development using xylenes followed by an IPA rinse. The lines are collapsing despite the presence of mechanical supports.

(1) higher resolution than with longer wavelengths and (2) energies commensurate with organic bond dissociation energies. Post-exposure UV ablation for development of a silicon resist has also been reported [23].

Our dry development technique and its comparison to wet development are illustrated in figure 1. Here, we use methyl acetoxy calix(6)arene (MAC6, TCI America) as this resist has shown high resolution in both electron beam [24, 25] and extreme ultraviolet (EUV) [26] lithography. After exposing the pattern with an electron beam, the development is accomplished by illumination with a focused 532 nm continuous wave (CW) laser (∼600 nm diameter spot size) under ambient conditions with the power on the substrate between 0.5–10 mW. The laser volatilizes the resist in the e-beam exposed areas (positive tone). In comparison, wet development in xylene [24] leaves a negative tone pattern due to insolubility of the e-beam exposed cross-linked resist. Collapsing features are apparent in the wet developed resist even with mechanical cross-struts (buttresses) [10]. In contrast, for the same pattern, the laser development process produces 11 nm trenches without collapse with high aspect ratios (>5:1).

For selective ablation, we have taken advantage of the elevated absorption of MAC6 upon the e-beam exposure. MAC6 shows strong absorption peaks at UV wavelengths (figure S1a in the supplementary data available at stacks.iop.org/Nano/23/185301/mmedia). We investigated visible regions of low absorption to maximize the ablation selectivity between the exposed and unexposed film. In the visible regime, the UV–visible spectrum of e-beam exposed (2 mC cm^{-2} at 10 keV) MAC6 shows an appreciable increase of absorption (figure S1b in the supplementary data available at stacks.iop.org/Nano/23/185301/mmedia). Best ablation selectivity was achieved with 532 nm light and was used exclusively for the experiments (see further discussion in supplementary data available at stacks.iop.org/Nano/23/185301/mmedia). Beyond selectivity, working with 532 nm has additional advantages in that the resist dry development process could be performed on polymer underlayers and substrates most of which typically do not have absorption around 532 nm.

We performed the development by laser irradiation in a micro-Raman setup, therefore having access to *in situ*, time resolved Raman and photoluminescence spectra during the ablation process. Raman spectra of unexposed and e-beam exposed films are shown in figure 2(a). In the unexposed films, distinct Raman peaks are noted. In contrast, the electron beam exposed film evidenced strong photoluminescence

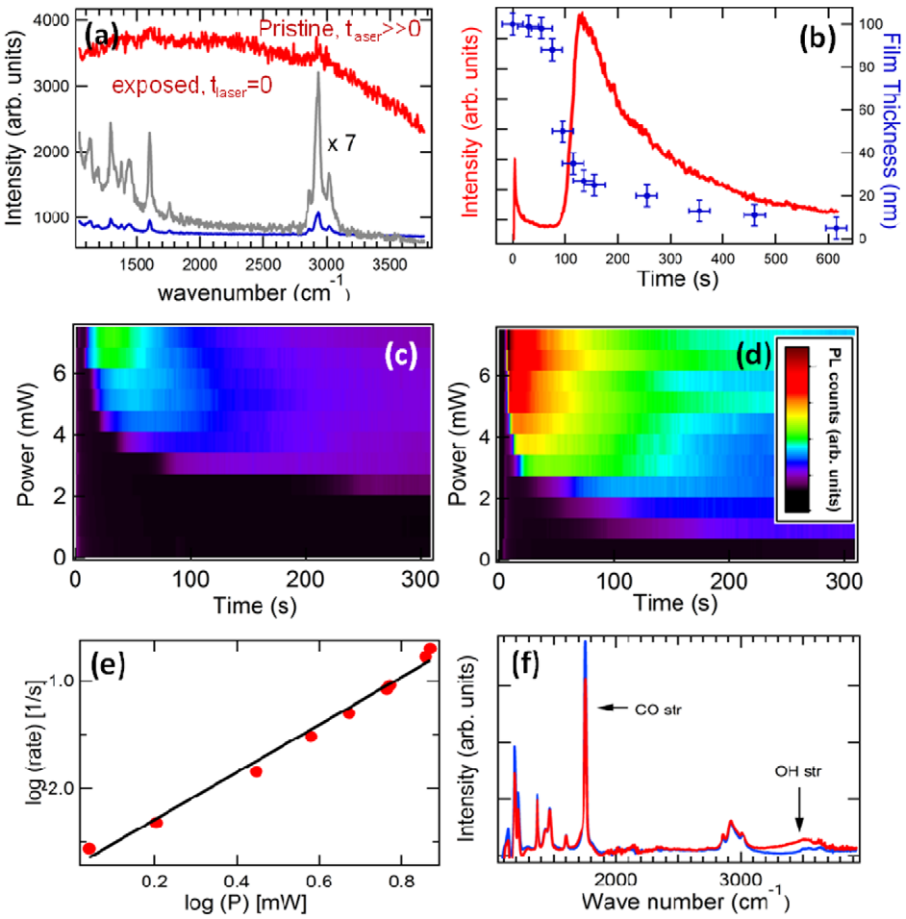

Figure 2. (a) *In situ* characterization of laser development processes using Raman spectroscopy; the Raman signal from exposed (red curve) and unexposed films (blue curve). (b) Correlation of the PL signal and ablation in pristine films; integrated (from 1800 to 2700 cm^{-1}) photoluminescence (red curve) is compared with the measured film thickness (blue curve). ((c), (d)) PL signal (color scale on the right) as a function of time and power for unexposed (c) and e-beam exposed MAC6 films (d). (e) Slope of the log/log plot of the ablation onset versus power, showing that the onset of ablation is a two-photon process. (f) FTIR spectra of unexposed (blue) and e-beam exposed (red) films. The e-beam exposure had caused the resist to lose carbonyl groups while forming hydroxyl units.

(PL) that hampered observation of the weak Raman signal features. With longer laser exposure times, we found that the unexposed films also exhibited similar PL. The integrated time dependent PL intensity for unexposed films was monitored and a typical curve is shown in figure 2(b). As illumination begins, there is an initial high luminescence signal that drops off within seconds which is followed by a period with no PL signal. During this time, Raman peaks were detectable (i.e. the blue curve in figure 2(a)). With time, a strong luminescence signal develops, masking Raman features. The luminescence reaches a maximum and then starts a gradual decrease. The film thickness in the illuminated area, as measured via AFM at various times (figure 2(b), blue crosses), shows that ablation starts at the onset of the main PL signal,with ∼80% of the film removed at the PL signal maximum. Hence, the onset of luminescence can be used as a monitor of the film ablation in MAC6. The long delay in the ablation time is henceforth called incubation.

The effects of laser power on the PL signal for unexposed and e-beam exposed films are shown in figures 2(c) and (d). For the unexposed films, at each power there is an incubation period which is represented by the black area of the map (figure 2(c)). With increasing power, this incubation time is shortened. In contrast, at the same laser powers, films pre-exposed using an e-beam flood gun (figure 3(d), e-beam dose = 2 mC cm^{-2}, 10 keV) have much shorter incubation times. Hence, the selectivity in the dry development of the patterned resist is provided by an accelerated ablation of the e-beam exposed areas which can be achieved with 1–2 s of power (at the same power, unexposed film requires ∼30 s to burn).

Clearly evident from figures 2(c) and (d) is the non-linearity of the ablation onset with power. To quantify this issue, we measured the incubation time at each power. A photon order plot of incubation rate versus laser power indicates the number of participant photons responsible for the incubation process via the slope [27, 28]. We found a slope of $n = 2.2 \pm 0.1$. This has two important implications: (1) the process is predominantly photochemical as photothermal ablation is a one-photon process; and (2) the incubation process has strong power density dependence. Typically, we used powers below 3.8 mW at a spot size of $\sim 2.8 \times 10^{-9}$ cm^2 to give power densities below 1.34 MW cm^{-2}, a value

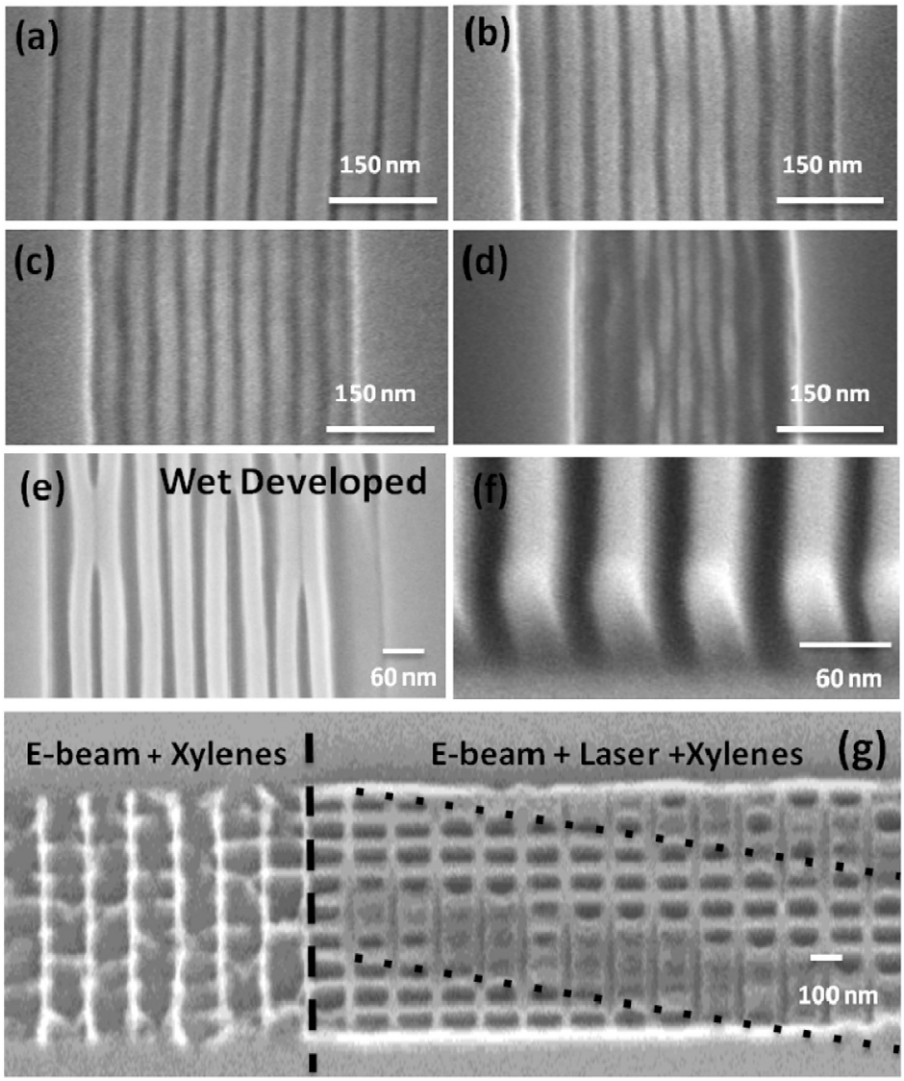

Figure 3. SEM images of laser exposed and wet developed patterns in 100 nm MAC6 films. ((a)–(d)) Top-down SEM images of 30, 25, 20, and 15 nm half-pitch laser developed features in 100 nm of calixarene. Laser development works down to 15 nm half-pitch features. (e) Wet developed features (30 s xylenes, IPA rinse) are completely collapsed. (f) 45° tilt cross-sectional view of a 30 nm half-pitch laser developed sample. (g) SEM micrograph of e-beam exposed and wet developed patterns (xylene development). The part of the pattern exposed only to the e-beam is underexposed, leading to a partially soluble pattern and thus poorly formed features (left), while laser exposure (below the ablation threshold) of the e-beam exposed pattern (right) prior to wet development further cross-links the resist (right). The dotted black lines show the path of the laser beam through the pattern.

commensurate with typical polymer ablation processes [21, 22]. The ablation was accomplished with 1–2 s per laser spot.

FTIR spectra of e-beam exposed and unexposed films are compared in figure 2(f). The most notable changes are the reduction of the carbonyl stretching mode at 1755 cm^{-1} and the appearance of a new broad peak at 3100–3600 cm^{-1}. These changes suggest that under the e-beam exposure, MAC6 loses some of its carbonyl units while forming new OH groups.

In fact, Kalumus and Hercules [29] have shown that phenol acetoxy does not photoluminesce while phenol does. Hence, a plausible explanation for the appearance of PL in the *in situ* Raman spectroscopy (figure 2(a)) is the removal of the acetoxy groups by e-beam or laser methods, to form phenol constituents. Furthermore, Kozowa *et al* [30] have shown that aromatic OH_2^+ formed from ionization of aromatic OH in deprotected chemically amplified resists is long lived and is responsible for an increased absorption at 532 nm wavelengths. On the basis of those findings, we surmise that the formation of aromatic OH in the e-beam treatment followed by aromatic OH_2^+ is in part responsible for the change in optical absorption leading to selective ablation. Furthermore, it indicates that the dry development method can be extended to chemically amplified resists with deprotected aromatic OH groups. In fact, our preliminary work with chemically amplified poly((t-butoxycarbonyl)oxy)styrene supports this hypothesis, as it shows strong ablation when deprotected, while at the same powers, it shows no ablation while protected. Detailed investigations of ablation mechanisms are under way and will be discussed in a future publication.

We have explored the limits of the laser dry development for patterned features and figure 3 summarizes the resolution that we have achieved to date. Laser developed line array patterns with varying half-pitches from 15 to 30 nm are shown in figures 3(a)–(d). Lines were written in a single pass with a line dose of 54 nC cm^{-1} and an e-beam width of ∼3 nm full width at half-maximum. A typical laser exposure time was in the range of 1–2 s per laser pixel of 600 nm diameter. The dry development method shows well resolved patterns down to 20 nm half-pitch at ∼4× less dose than xylene developed patterns. At 15 nm half-pitch, although the outer pattern features collapse to the sides, the central region is well resolved and shows the impressive potential of this groundbreaking development method. We show for comparison a wet developed pattern at the same resist thickness (figure 3(e)). Pattern collapse decreases with increasing pitch, but even the least challenging pattern investigated (30 nm half-pitch and a line dose of 220 nC cm^{-1}) collapses with xylene wet development. A cross-sectional SEM image (45° tilt) of a 25 nm half-pitch sample exposed and developed is shown in figure 3(f). The line dose here was 42 nC cm^{-1}. The ablated portions appear clear to the bottom of the pattern which is crucial for pattern transfer. Finally, we demonstrate an alternative use for laser exposure when pattern collapse can be avoided (e.g. very thin resists or less dense patterns). The e-beam and laser exposures are performed sequentially at sub-ablation threshold and followed by a wet development to produce a negative pattern (figure 3(g) right). The dotted line shows the path of the laser beam. Interestingly, the strong effect of the laser power density becomes evident. The areas where the center of the Gaussian laser beam hits (above the dotted lines) have begun to ablate, while the tails of the laser beam have only strengthened the cross-linking of the material. At this same dose, the e-beam alone produces an underexposed pattern (figure 3(g) left). With this approach, the time needed for the primary exposure tool (here, the e-beam) is decreased. Here we achieve a ∼4× decrease in dose. This experiment also shows that cross-linking is one of the chemical changes occurring when the e-beam film is hit by the laser. At laser doses above the ablation threshold this cross-linked material is eventually able to ablate selectively over the small molecule pristine film.

In conclusion, we report on a novel laser ablation development method which works in lieu of wet development for high resolution resist patterning. The increased optical absorption of the e-beam exposed over the unexposed regions provides selective laser ablation of the beam exposed areas in positive tone. Although laser development is combined with e-beams herein, the technique is expected to work with other high resolution radiation sources such as 193 nm immersion, EUV or ion beams. We explored the key parameters for achieving selectivity, which include laser wavelength, high resolution patterning dose, laser power and illumination time. With a 532 nm CW laser, we have demonstrated high aspect ratio resist features down to 15 nm half-pitch. Laser ablation was able to achieve selectivity with ablation time of 1–2 s per laser pixel of 600 nm. In addition, we found that underexposed high resolution electron beam patterns can be subsequently selectively laser cross-linked in the exposed region to further improve the electron beam dose threshold for negative tone patterning. More importantly, with this new technique, pattern collapse, a huge obstacle for high resolution lithography, has been overcome. We are currently investigating the underlying chemical mechanisms for laser film cross-linking and selective ablation, as well as extending the process to other resist systems, including chemically amplified resists.

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