Dry photolithography through ultraviolet radiation-induced photo-etching of polymethyl methacrylate

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ABSTRACT

We describe a technique for photo-patterning polymethyl methacrylate (PMMA) resist films that does not use a wet development step. 254 nm deep ultraviolet radiation from an ordinary mercury discharge lamp was used to both chain scission and remove PMMA in a single step lithographic process. PMMA films several microns thick can be patterned through this technique. The patterned film can also be directly used as a structure, by itself, for applications in microfluidics etc. Our process relies on a synergistic effect that greatly accelerates the loss of PMMA when it is simultaneously heated close to its glass transition temperature and irradiated with 254 nm radiation. Furthermore, we also describe a secondary exposure effect in this process that originates from electrons that are generated through a photoelectric effect at the PMMA-substrate interface. This gives rise to a proximity effect analogous to that encountered in conventional electron beam lithography.

Conventional lithography techniques generally employ a two-step process involving a resist exposure step followed by pattern development in a suitable wet developer. The exposure can be performed by irradiation with either electromagnetic radiation or charged particles. In either case, the latent image formed in the resist is subsequently developed with either a chemical or physical wet resist dissolution process. Here, we introduce a variant of deep UV (DUV) photolithography that allows patterns on a mask to be directly reproduced in a resist film without the need of a conventional resist development step.

The central idea behind this technique is to use DUV radiation itself to selectively erode a thin polymethyl methacrylate (PMMA) resist film in a pattern defined by the spatial exposure of the resist film. The exposing UV light field is spatially configured by passing light from a DUV source through a binary chrome-on-quartz mask, just like in ordinary photolithography. The difference from conventional photolithography lies in the fact that not only a latent image is formed in the resist but, with sustained exposure, the resist material is gradually lost from the exposed locations. Thus the exposure itself leaves the resist patterned in the shape of the mask pattern – no separate development step is required. Some of the concepts underlying this technique have been known for some time but have not been carried out together as a useful integrated micro-patterning process [1]. Our work demonstrates a clearly-defined integrated process of great practical value for micro- and nano-fabrication. A very significant finding is that the PMMA removal process is synergistically aided by heating the film, which enhances the rate of film thickness reduction several times, that is not

achievable with UV radiation exposure alone. We show that several microns thick PMMA films can also be easily patterned with this technique and even 3D topographic structures can be produced. Finally, we show that the optical patterning process is aided by a secondary electron exposure, caused by photo-electrons ejected from the substrate.

In the lithography process described here, a PMMA resist film is exposed to 254 nm UV radiation through either a metal-aperture shadow mask or a conventional photomask. The UV source can be a simple cold or hot cathode low pressure mercury discharge tube. Depending on construction, many such tubes generate principally the 254 nm mercury resonance line while some tubes also generate some 365 nm i-line radiation. On exposure to 254 nm UV radiation, the PMMA film gets gradually thinned down through four different processes. All of them are consequences of the fact that DUV irradiation causes PMMA to chain scission. The scission yield is very small at the 365 nm i-line wavelength but begins to climb significantly once the exposure wavelength decreases below 300 nm [2]. At around 260 nm and below, the quantum yield of photon-induced bond chain scission increases to such an extent that the process becomes useful for lithography. This process generates both short chain fragments and small simple molecules [3]. The film then loses mass through three mechanisms: (i) loss of small volatile molecules, such as CO, CO_2, CH_4 and H_2O, (ii) volatilization of somewhat bigger molecules by their attachment to a free radical and (iii) direct evaporation of PMMA fragments that get energised through absorption of UV photons, followed by energy equipartition throughout the chemical bond. All of these processes cause loss of film material and thus lead to film shrinkage. A fourth mechanism that also leads to film shrinkage, but without loss of film material, is the compaction of PMMA due to chain scission. Fragmentation of long polymer chains and loss of

material, as described above, results in the formation of internal voids in the PMMA film. This consequent subsidence leads to the film material becoming thinner. We studied the dependence of PMMA removal rate on the molecular weight of PMMA by carrying out experiments on nearly mono-disperse PMMA of three different average molecular weights: 120,000 g/mol, 350,000 g/mol and 996,000 g/mol. Their film thickness reduction rates with steady irradiation at room temperature, using 254 nm radiation at 9 mW/cm^2, were found to be 36.9, 21.3 and 10.2 nm/h, respectively.

PMMA films can very slowly evaporate when heated in air. The rate speeds up considerably near the glass transition temperature, T_G. Fig. 1 shows the loss of PMMA film thickness when heated to 60 °C in air for different lengths of time. This figure also depicts the loss of PMMA when films, at room temperature, are irradiated with steady UV radiation (254 nm) at a power density of 9 mW/cm^2. Thus, both heating and suitable UV irradiation can cause loss of PMMA. The dashed line shows the simple addition of these plots. We found that the loss of PMMA film thickness is greatly accelerated when a film is both heated and UV-irradiated at the same time (see the green line and round markers in Fig. 1). This clearly implies a synergy between the thermal and optical processes that is effective in removing PMMA. Thermal loss of PMMA is greatly accelerated by simultaneous UV-irradiation which creates short chain fragments that are readily removed with thermal energy. To benefit from this synergy, we heated our PMMA-coated substrates to 90 °C during DUV exposure.

We investigated the effect of UV exposure on PMMA films at multiple temperatures (ambient temperature, 60 °C and 90 °C) and for different lengths of exposure time at 9 mW/cm^2 incident UV intensity. 2.5 μm thick PMMA resist films were prepared by spin-coating a solution of 120,000 g/mol PMMA in ethyl lactate onto silicon chips. In each case, the remaining thickness of the thin films was measured and the results are shown in Fig. 2 where the percentage of remaining PMMA thickness has been plotted against UV exposure time in hours. Trend lines have been added in this plot. Data points plotted without trend lines are for experiments where a wet development in IPA was carried out. Less exposure time is needed for complete film removal with wet development. It can be seen that temperature has a very significant effect on the loss rate of PMMA. There seem to be two distinct regimes of resist material loss - bulk and thin film. The bulk regime refers to the linear proportion of the trend line where the PMMA properties are similar to bulk properties of the material. Greater exposure doses contribute to larger amounts of material loss. As the film height reduces further, to approximately 500 nm of thickness, the evaporation rate slows down very rapidly. A drastic reduction in evaporation rate occurs in the thin film regime. The evaporation rate, in this regime, slows due to two
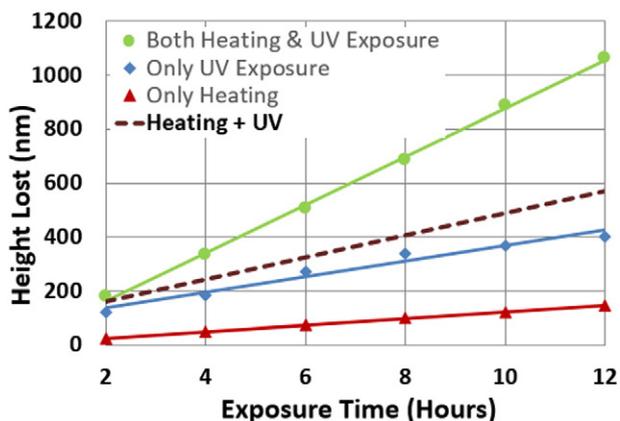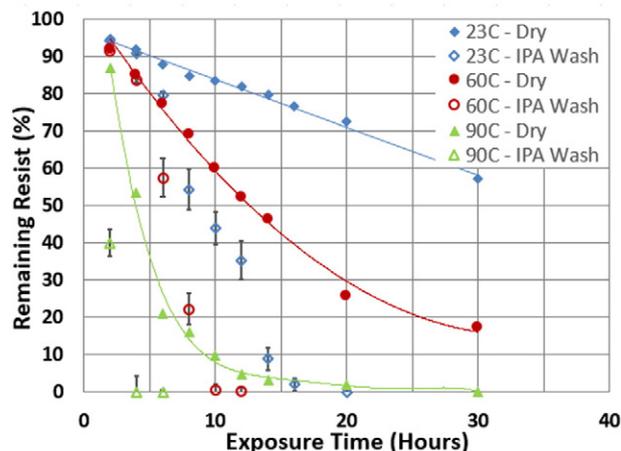

Fig. 2. Remaining 120,000 g/mol PMMA resist percentage versus exposure duration. For each temperature, the samples were measured twice; after exposure (labelled – 'Dry') and after a 2 minute ultra-sonic wash in IPA (labelled – IPA wash).

different mechanisms, compaction (mentioned earlier) and thin film effects. This latter effect is due to the different morphological structure of PMMA close to the substrate surface [4]. PMMA adjacent to substrate surface is known to possess higher T_G compared to bulk material and shows greater tenacity [5]. Since the evaporation rate drastically slows down around 500 nm, compaction is likely the more dominant mechanism in this process as the morphological effects do not appear until the film is less than 50 nm thick. Long enough UV exposure removes even thick PMMA films and the rate of film loss is greatly accelerated at elevated temperatures. A temperature of 90 °C is likely to be optimal, as it is high enough to remove PMMA at practical rates but still is below the T_G of PMMA so that the film maintains its rigidity and no pattern distortion is observed. Although we patterned quite large structures measuring several millimetres across in this work, the resolution of this technique is determined, primarily, by the resolution capability of PMMA which is known to be able to reproduce patterns down to only a few nanometres across [6]. We utilized a patterned shadow mask in this work. The samples were exposed for 14 h at 90 °C in ambient air. The correct duration of exposure is determined by the thickness of PMMA, the optical power of the source and the temperature maintained during exposure. Fig. 3(a) shows an optical micrograph of the PMMA, patterned with a wheel-and-spokes pattern.

Microscopy and surface conductivity measurements have shown that exposed areas are cleared all the way down to the substrate and there is no erosion of PMMA in un-exposed areas, thus providing extremely high contrast. While we used 2.5 micron thick PMMA film, the film thickness can be easily increased, at the expense of longer exposure times, to pattern much thicker films. Furthermore, we also found that co-polymers of PMMA with polystyrene (PMMA-co-PS) also functions in this role in much the same way as PMMA itself while providing higher resistance to dry etch plasmas during pattern transfer. After exposure, the sample was dry-etched for 4 min in a BenchMark 800® inductively-coupled reactive ion etcher. The reactive ion etch process utilized 30 sccm of SF$_6$ flow, at 1.33 Pa, to effectively etch the silicon substrate, exposed through patterned-PMMA. The RF power was set to 100 W, in order to sustain the plasma during the process and the DC bias was 300 V. The silicon was etched to a depth of 2.7 μm at an etch rate of 680 nm/min and an optical micrograph of the etched sample is shown in in Fig. 3(b).

We have observed an interesting secondary exposure of PMMA from electrons that are ejected from the substrate. These electrons are ejected due to a photo-electric effect, as UV photons penetrate the resist PMMA film and hit the silicon surface. A direct optical transition model for photoelectric effect from silicon surfaces has been described earlier [7]. These photoelectrons cause chain scission of PMMA, thus creating a

Fig. 1. Height loss in nm for 120,000 g/mol PMMA films due to DUV exposure, thermal exposure, and both thermal and DUV exposure together, while varying the length of exposure. The dotted purple line represents the simple addition of DUV exposure height loss and thermal exposure height loss.