Low Cost PMMA based photo–masks for 3D grey scale micro–structuring applications

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ABSTRACT

The transfer of a three dimensional grey–scale pattern from a polymer composite to a photoresist has been demonstrated. The grey scale structure was fabricated using variable dose electron beam lithography. The optical transparency of the electron beam resist was reduced by the addition of Al_2O_3 and TiO_2 nanoparticles. The reduction in optical transparency of this composite was due to the radiation scattering effects of the poly crystalline nanoparticles. By increasing the nanoparticle density, the overall transparency of the composite is reduced.

Keywords: PMMA, nanoparticles, photoresist, 3D grey scale, electron beam lithography.

1 INTRODUCTION

Grey–scale lithography is a useful technique for fabricating three dimensional structures in a polymeric thin film [1] and can be achieved by variable dose methods or fixed dose methods [2]. Utilizing structured photoresist as an etch mask for example can enable a three dimensional structure to be transferred to a substrate material such as silicon; anisotropic dry etching is one method. However, fabricating the grey–scale mask in the first instance is technically challenging and time consuming [3]. This is particularly significant in that all etch masks of this type are single use. Transferring the three dimensional grey–scale structure from the electron beam resist to a standard photoresist enables multiple structures to be made from a single mask. Polymethylmethacrylate (PMMA) based electron beam resist is highly transparent at wavelengths associated with the exposure of photoresist. This material alone would not be suitable as a photolithography mask. However, it is possible to modify the optical properties of this polymeric film through the homogeneous dispersal of nanoparticles.

2 EXPERIMENTAL

The PMMA composites used in this study were obtained by the homogeneous dispersal of Al_2O_3 and TiO_2 nanoparticles in PMMA. Samples were prepared by adding 10mg through to 200mg of nano–particles to 1.6g of PMMA. The nano–particles were pre–wetted in 0.5ml of methanol to produce a particle suspension before being mixed with the PMMA. These composites were then spun onto 25mm×25mm borosilicate glass microscope cover slips. The cover slips were sputter coated with a few nm of gold; whilst necessary for electron beam exposure, provided additional adhesion qualities. A spin cycle of 6000rpm for 45 seconds was followed by a soft–bake at 180°C for 3 minutes.

The optical transmission of the composite films at a wavelength of 365nm was obtained using a Jenway spectrophotometer.

The three dimensional structuring of the resist composite was achieved through variable dose exposure using the Raith 50. The exposure dose was modulated from 10 through to 30μA/cm^2 in increments of 5μA/cm^2. The composite resist was developed using MIBK developer and IPA solvent in the ratio 1:3.

These composite photo-masks were used to expose Microposit S1813 positive photoresist (see figure 2–0). This was spun onto silicon substrates at 6000rpm for 45 seconds yielding a photoresist thickness of typically 1.1μm. The composite masks were then placed in contact with the S1813 and a typical 6 second UV exposure using a Karl Suss mask aligner. The sample was then developed for 40 seconds at room temperature. The developer solution was 2401 developer and water in the ratio 1:10.

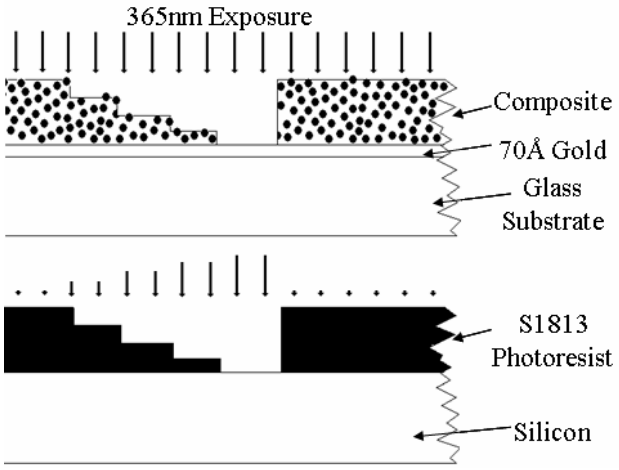

Figure 2–0: A schematic of the contact printing process; the photoresist is show 'as developed'.

3 RESULTS

3.1 Optical attenuation and scattering

The optical transmission at 365nm as a function of nanoparticle density for the composite sample is shown in figure 3–0. The optical transmission is inversely proportional to nanoparticle density over the range shown and becomes 90% transparent for PMMA alone. Note: the borosilicate glass substrate alone is at 96%.

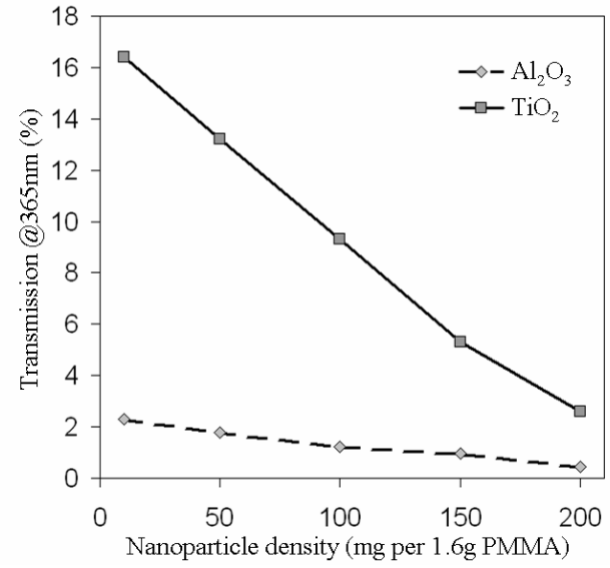

Figure 3–0: Optical transmission as a function of nanoparticle density for both types of composite.

Comparing both the Al_2O_3 and TiO_2 nanoparticle composites, it is evident that the resultant reduction in transmission is greater with Al_2O_3 than with TiO_2. This enhanced opacity through nanoparticle dispersal is a result of particulate scattering rather than by direct absorption [4,5]. In simple terms, the extinction or attenuation of incident light is given by

$$I_t = I_i \exp(-\alpha_{ext} T), \quad (1)$$

where I_i is the incident intensity, T is the thickness of the composite resist and α_{ext} is the extinction coefficient. The standard definition is given by

$$\alpha_{ext} = y\, C_{ext} = y\, C_{abs} + y\, C_{sca}, \quad (2)$$

However, having determined scattering to be the dominant process, the extinction coefficient for an ensemble of randomly sized particles is given by

$$\alpha_{ext} = \sum_j y_j C_{sca,j} \quad (3)$$

where y_j is the number of particles of type j per unit volume with $C_{sca,j}$ being the scattering cross section. The extinction coefficient α_{ext} for the Al_2O_3 and TiO_2 composites studied ranged from ~4μm^{-1} to ~7μm^{-1} and ~2μm^{-1} to ~5μm^{-1} respectively (this assumes a typical 'spun on' PMMA composite thickness of 0.8μm). The optical transmission of the resultant thin film composite is highly sensitive to thickness variations. Subsequent variable dose electron beam exposure can produce patterns of variable thickness. Micro–structuring a thin film in this way can result in a grey–scale optical mask.

3.2 Grey-scale lithography

The electron beam exposure dose parameters have been characterized and the resultant PMMA thickness following development is shown in figure 3–1. It is clear that as the exposure dose increases the composite resist height decreases ; this is reasonably linear over the range shown.

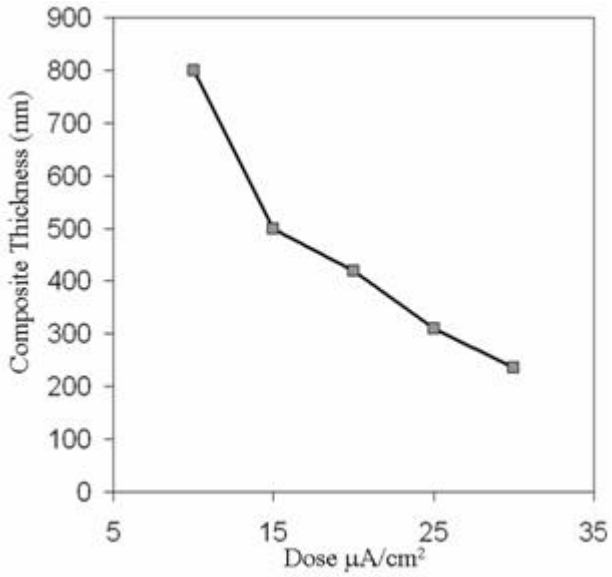

Figure 3–1: Resultant PMMA thickness following development as a function of exposure dose.

In order to test the performance of the composite films during photoresist exposure a number of test samples were prepared consisting of borosilicate glass substrates coated with composites of different nanoparticle density. This experiment is directly analogous to that described above, whereby S1813 photoresist is subjected to a variable dose of UV radiation and the thickness following development is measured. The results obtained are given in figure 3-2 following a 6 second exposure in a Karl Suss mask aligner. Again, the variation in S1813 thickness is proportional to nanoparticle density over the range shown.

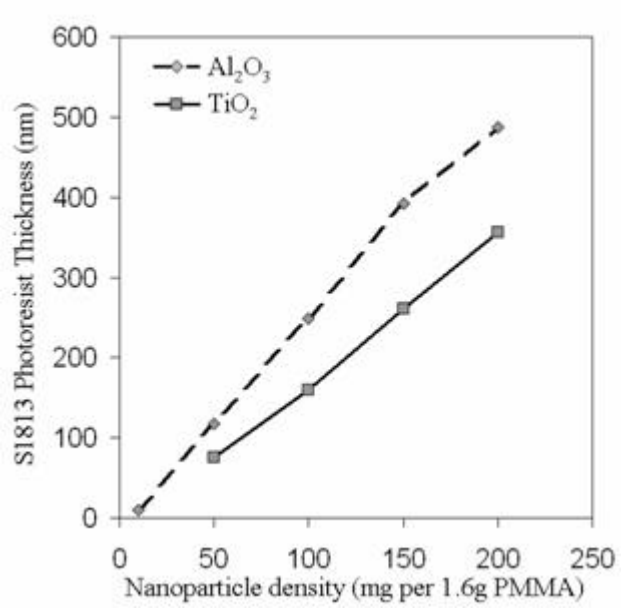

Figure 3–2: Developed S1813 photoresist thickness as a function of particulate density in the composite.

4 ANALYSIS

Feature definition in the exposed composite electron beam resist is next considered. A test pattern was prepared, consisting of a sequence of five 50µm squares, each exposed at a different dose increasing from 10 – 30µA/cm^2 in steps of 5 µA/cm^2. The composite in this case consisted of 10mg of Al_2O_3 nanoparticles dispersed in 1.6g of PMMA. The particle size averaged 30nm. The 'spun on' thickness of the composite was around 800nm. This particular sample represents a 'worst case'; here a surfactant was not used in the sample preparation. As a result, some particulate clumping was observed in the composite film. The optical microscope image below (figure 4–0) shows the exposed squares. When viewed in color the top row of squares change from red on the left, through green, to blue on the right. This is due to thin film interference effects under white light illumination. The rows of squares below were exposed at doses higher than 30µA/cm^2 resulting in the complete removal of the PMMA composite following development.

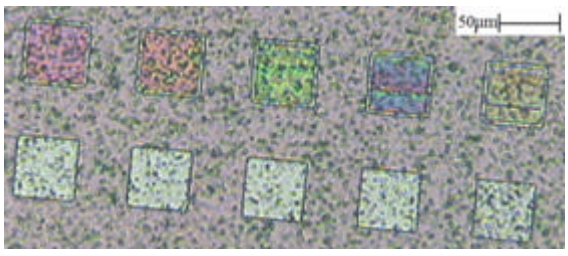

Figure 4–0: PMMA composite following development and variable dose exposure.

The variation in thickness of the resultant thin film across this top row of squares was measured by a Detak stylus profileometer. The trace from this apparatus is shown in Figure 4–1.

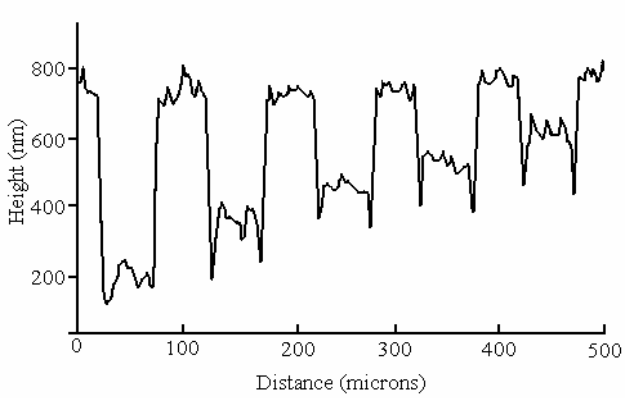

Figure 4–1: 50µm 3D grey scale composite resist profile measured with the Detak profileometer.

Important work by Fenzl [6] has formed the basis of an extensive study on the pre wetting of the nanoparticles and surface adhesion properties; this will be discussed in a future publication.

Initial tests on the transfer of the structured composite pattern into S1813 photoresist were carried out. A photoresist coated silicon sample was exposed in the mask aligner by the contact printing method, utilizing the patterned composite mask described above. A standard 6 second exposure was used followed by a standard development stage. Whilst the mask composite used in this case had the lowest nanoparticle density, the resultant photoresist showed some degree of grey–scale structuring (see figure 4–2 below).

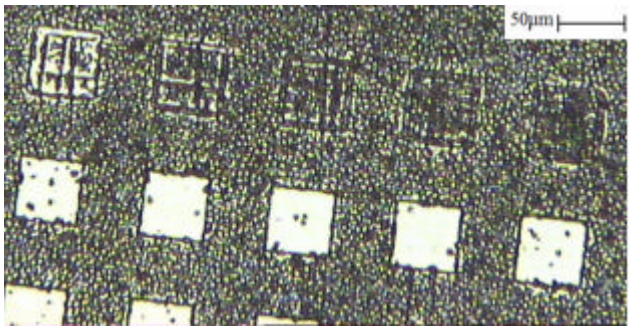

Figure 4–2: The S1813 grey–scale structured photoresist on silicon.

The poor choice of PMMA composite for the photo–mask resulted in a general 'over exposure' of the photoresist. Some degree of grey–scaling is evident in this image; the top row of squares shows a decrease in contrast with the

surrounding photoresist going from left to right. The overall resultant photoresist thickness was less than 100nm in this case. An attempt was made to measure the structure using the Dektak; however, the system used did not have sufficient resolution.

5 CONCLUSIONS

The fabrication of simple low cost grey scale photo–masks has been demonstrated using the technique described. The optical properties of the PMMA nanoparticle composites were determined by use of a Jenway spectrophotometer. Optical scattering is the dominant attenuation mechanism with nanoparticles of Al_2O_3 producing a higher overall attenuation as compared with TiO_2. Grey–scale structuring of the composite thin films using a Raith 50 electron beam lithography system has been demonstrated. The transfer of this structure into the photoresist has seen some limited success; however, in retrospect, the higher density nanoparticle composites should have been used in this aspect of the study. The effectiveness of the higher density composites has been demonstrated however. A series of composite masks with increasing nanoparticle density, were used to expose photoresist. The thickness of the developed photoresist films was shown to vary linearly with nanoparticle density over the range described.

6 ACKNOWLEDGEMENTS

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