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Surface charging suppression using PEDOT/PSS in the fabrication of three dimensional structures on a quartz substrate

K. Mohamed, M.M. Alkaisi *, R.J. Blaikie

MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Electrical and Computer Engineering, University of Canterbury, Private Bag 4800, Christchurch 8020, New Zealand

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ABSTRACT

Pattern writing on insulating materials (e.g. quartz) using electron beam lithography (EBL) is a challenging task and it is even more difficult when the pattern is three dimensional (3D). Surface charging trapped on insulating substrates may deflect the electron beam during electron beam pattern writing causing undesired effects.

In this work, the surface charging has been suppressed by top coating with water soluble conductive polymer layer using poly (3,4-Etylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS). The 3D masking profiles are created on a negative tone photoresist (Microresist, ma-N2403) using Raith150 EBL tool with variable dose controlled beam exposure. The 3D patterns have been transferred onto the quartz substrate by single step reactive ion etching (RIE) with suitable resist to substrate selectivity.

We have demonstrated the fabrication of 3D geometrical shapes such as pyramids, hemispheres, and cones with dimensions down to 300 nm using this technique without any surface charging effects.

1. Introduction

Ultra-violet curable nano-imprint lithography (UV-NIL) technique is a promising technique for fabricating nanostructures with high resolution, low cost, high throughput and capable of three dimensional (3D) patterning. In this technique, the transparent mold is lightly pressed on to the UV curable resist and exposed to UV light source for curing. The replication of the mold pattern is realized upon releasing the mold from the quartz substrate. The process involved in making 3D molds on transparent substrate such as quartz is a very challenging task, owing to surface charging and pattern transfer requirements. The 3D and multilevel profiles can be created on negative resist using a variable e-beam dose control method [1] of electron beam lithography (EBL). During a continuous e-beam exposure, negative electron-charges are created and secondary electrons are emitted, the charges trapped in the resist and insulating materials will build up to a level that may bend the electron beam leading to a distorted written pattern [2,3]. The insulating materials charge up negatively or positively depending on the conditions during the e-beam exposure.

There are a number of methods that can be employed to overcome the surface charging effects. For example, a thin metal layer is normally used as top conductive coating deposited on top of the resist surface to facilitate charge dissipation and prevent charge build up. However, removing the metal layer at a later stage is troublesome, as removing it by using wet etching with an acidic solution is not possible for this work because the reaction of the acidic solution with the negative photoresist will crosslink the polymer chains [4]. On the other hand, removing the metal layer by plasma etching will harden the photoresist surface causing difficulties in developing the pattern at a later stage. Another method is to write the patterns using a critical e-beam energy technique [2,5]. In this method, an e-beam exposure environment is optimised to yield neutral charges on the photoresist surface by critically determining the e-beam acceleration voltage that results in negative/positive charge neutralization on certain resist thicknesses. However, this might be quite troublesome for uneven photoresist surfaces. Another disadvantage of this method is that the low voltage acceleration makes the e-beam spread horizontally. This limits the smallest feature size that could be created owing to proximity effects. Three dimensional features down to 1 μm were demonstrated in our previous work [5] using this technique.

Conducting polymers, particularly the soluble derivatives, are other potential alternatives as charge dissipators for EBL writing on insulating materials [6,7]. This work proposes using a water soluble conductive polymer, poly (3,4-Etylenedioxythiophene)/poly(styrenesulfonate) PEDOT/PSS as the top conductive coating on the negative photoresist layer. Removing the water soluble conductive polymer layer is much easier compared to removing a metal layer. PEDOT/PSS can be removed by rinsing with de-ionised water (DIW) after the e-beam exposure prior to the development process.

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* Corresponding author. Tel.: +643 3516618.
E-mail addresses: maan.alkaisi@canterbury.ac.nz, kmo39@student.canterbury.ac.nz (M.M. Alkaisi).

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2. The mold fabrication

Quartz substrates were cleaned more successfully using low volatility NMP (*N*-methyl pyrrolidone) solvent and this is found to give better results compared to cleaning in acetone, methanol, and IPA. The quartz samples were soaked in the NMP solvent for 15 min at a temperature of 45 °C followed by an ultrasonic bath for 5 min. They were then rinsed with DIW, blown dry with nitrogen, and baked at a temperature of 185 °C for 15 min. The 3D mold fabrication process flow chart is shown in Fig. 1. The negative tone photoresist from Microresist Technology Gmbh, ma-N2403 was spun coated on the quartz substrate at 3000 rpm for 30 s, and pre-baked in the oven at a temperature of 95 °C for 30 min to achieve a 600 nm layer thickness. The conductive polymer from Sigma–Aldrich, PEDOT/PSS was then spun coated on top of the ma-N2403 resist at 5000 rpm for 1 min, and baked on a hot plate at a temperature of 90 °C for 2 min to achieve a thickness of about 30 nm.

Raith 150 EBL tool was used for exposing samples with e-beam 3D pattern writing. Fig. 2 shows SEM images for quartz substrates exposed with an e-beam at an acceleration voltage of 20 keV with a 20 μm aperture. Fig. 2a shows an SEM image of substrates coated with negative photoresist only, without the conductive polymer layer; these display the characteristic bright area of built up charges. No objects can be resolved for imaging or writing under the influence of surface charging. Fig. 2b shows an SEM image of a substrate coated with negative photoresist and the proposed top conductive coating (PEDOT/PSS) after it has been exposed with an e-beam. No charging effects were observed as evident shown by the confined 20 nm dot at the resist surface where surface charging was significantly suppressed. Fig. 2c illustrates the schematic diagram of the electron path that leads to secondary electron emission and built up charges. In comparison, Fig. 2d illustrates the schematic diagram of the electron path with the existence of a PEDOT/PSS conductive layer. Most trapped and built up electron-charges are grounded through the PEDOT/PSS layer.

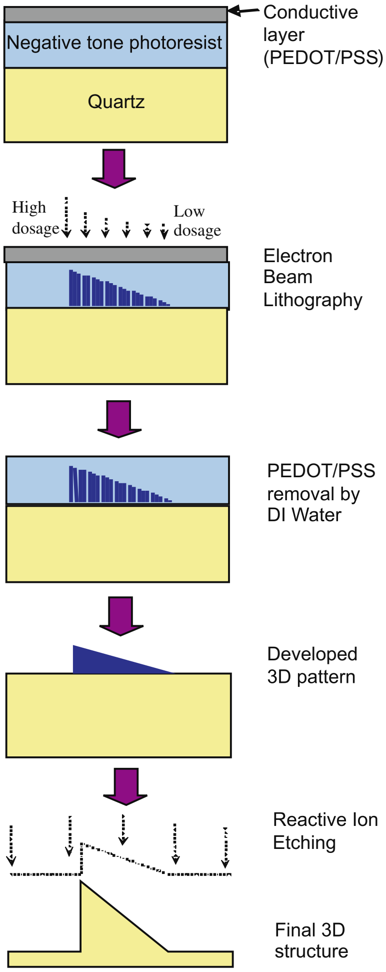

Fig. 1. Schematic diagram of the 3D mold making process on quartz substrates.

The single pass line (SPL) pattern writing scheme was utilized for 3D patterning with line dosage starting at 0.6 pC/cm up to 42.0 pC/cm. Fig. 3a shows an example of the 3D pattern writing scheme for a 300 × 300 nm^2 base pyramid. It was created using e-beam writing on the negative resist by routing the multiple SPL parallel paths with various dosages assigned for each SPL (paths 1–6). The spaces between each SPL route ranged from 20 to 30 nm. Fig. 3b shows an AFM image of the developed 300 × 300 nm^2 base pyramid where the height is 350 nm. To achieve the desired 3D profiles, proximity effects must be minimised unless a proximity correction system is in place. Without the proximity correction system, dosage optimisation has to be carried out manually for 3D patterning.

In 3D patterning, the developed resist height at a particular spot is determined by the magnitude of resist crosslinking at that location due to direct e-beam exposure plus the proximity effects from adjacent exposures. At lower voltage acceleration of below 10 keV, the spread of the e-beam is quite large (up to 3 μm), hence, the developed resist height at a particular spot is heavily affected by multiple proximity effects caused by line exposures near to the spot. Exposing a line with low dosage does not necessarily produce a low resist height if the surrounding lines are exposed with high dosages. Manual optimisation of line dosages in order to achieve certain resist height in 3D pattern requires a long iteration experiment process owing to multiple proximity effects from surrounding exposures.

In this work, a higher voltage acceleration of 20 keV has been exposed as compared to 6.5 keV used in previous work that followed the critical energy method [5]. The advantage of exposing an e-beam at a higher acceleration voltage is that it will suppress the proximity effects on the surrounding exposure region, resulting in a better control over developed profiles, less time required for the dosage optimisation process and higher density 3D patterns are possible.

After the e-beam exposure, the sample was soaked in the DIW for 1 min and DIW rinsing was continued for about 30 s to ensure removal of the PEDOT/PSS layer, then blown dry with nitrogen. All samples were developed in a ma-D532 developer for 15 s at a temperature of 20 °C.

Finally, the 3D resist patterns are utilized as a 3D masking layer and the 3D pattern is directly transferred onto the quartz substrate by single step CHF_3/Ar reactive ion etching (RIE) using Oxford Plasma80 Plus etcher.

3. Results and analysis

Fig. 4a shows an AFM image of the ma-N2403 resist as a 3D masking layer after being developed in the ma-D532 developer. The highest point of this 3D pattern is about 300 nm. The resultant 3D profiles show no distortion from the designed shapes.

Fig. 4b shows an SEM image of the 3D structure on the quartz substrate after the RIE pattern transfer process with selectivity resist to substrate of 1:2. The height of the 3D structure at its highest point is about 600 nm.