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Patterning of photoresist by micro-holes with controllable physical dimensions via maskless photolithography

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Patterning of positive photoresist, coated on glass, with micro-holes via maskless photolithography was the subject of this study. The successful formation of micro-holes with controllable physical parameters on the homogenous photoresist was confirmed by optical microscope and profilometer measurements. Mainly, the effect of modulation and velocity of the laser on the spacing and diameter of micro-holes has been investigated. The comparison of the spacing-to-diameter (s/d) ratio calculated from the pattern with the smallest diameter and highest spacing to the one with the highest diameter and smallest spacing gives the result of 18-fold. For the pattern with the s/d ratio obtained by the lowest modulation and highest velocity, the circular shaped and well-defined micro-holes with 500 nm thickness, 10 µm diameter and varying spacing from 15 (bottom) to 30 µm (top) could be obtained successfully.

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1. Introduction

Glass and silicon are the most commonly used substrates in microelectronics technology. Micro-patterning of silicon is generally applied to obtain the “black-silicon” with a very low surface reflection, which is quite beneficial for the photovoltaic industry [1-3]. Meanwhile, the microstructures formed on glass behave as spots that manipulate the light such as focusing and redirecting. Generally, glass substrate decorated with microstructures is mainly preferred for micro-lens [4], biomedical [5], and solar cell applications [6-8].

The texturing process can be classified into two main categories; wet and dry etching approaches. Although wet chemical etching provides micro and nano-structure formation especially for silicon [9,10] a more controllable and clean process of surface texturing for both silicon and glass can be conducted by dry etching along with lithography. For instance, the usage of photolithography and the deep reactive ion etching (DRIE) together [11] is one of the most effective approaches to form microstructures with controllable shapes and dimensions. Indeed, it is achievable to obtain the microstructures with sizes varying from few hundred to few micrometers along with the shapes of pores [12], pillars [13], cones [14], etc. Here, the aim of the photolithographic process is to provide an appropriate mask before the etching process. The success of controlling the shape and dimensions of the microstructures depends mainly on usage of the mask with homogenous and well-defined pattern formed via photolithography. Therefore, it can be proposed that the appropriate masking is the vital starting step for a successful etching process [15].

The lithographic process can be carried out via a preprepared mask (masked lithography) or directly exposing the laser onto the photo-sensitive coating (maskless lithography) on the substrate. However, the high cost of masks decreased the interest in masked lithography. Additionally, the freedom in choosing the dimensions and shapes of the proposed microstructures has made the maskless lithography more attractive and preferable over the masked lithography [16].

To perform maskless photolithography, coating a photo-sensitive material called photoresist on the substrate is the first step. Then, the UV-laser (UV-lithography) [17] is shined on the photoresist to create the exposed and unexposed areas which define desired pattern on the substrate. After exposure, the substrate is immersed in a solution that selectively removes the photoresist areas whether exposed or unexposed. This process, which is required to reveal the pattern defined on the surface, is called developing [18]. The photoresist can be named as positive [19] or negative [20] based on the removal part during the developing process. The developer removes the exposed areas if the photoresist is positive, or unexposed areas if the photoresist is negative. Consequently, the pattern to be used as an etching mask is coated on the substrate and the further etching process can be carried out to decorate the substrate with microstructures [21].

Despite the widely usage of photoresist patterning during the maskless photolithography prior to the etching process, we noticed that, to our best knowledge, there is not any comprehensive study focusing directly on physical properties micro-circles such as diameter and spacing by tuning the laser parameters. Indeed, since successfully etching of microstructures on the substrate is directly related to the pattern of photoresist that can be controlled via UV-laser properties, we believe our study would make a remarkabele contribution to the literature. We preferably chose glass as substrate in this study since glass is widely used in many kinds of applications. To successfully decorate glass with microstructures, the first step to be achieved is to create a well-defined pattern on the photoresist coated on glass that would behave as a mask. Due to its benefits, maskless photolithography has been operated for the delineation of photoresist for patterning. For this purpose, the micro-circles were scribed on the photoresist under various laser parameters and the effect of the parameters on the physical properties of the micro-circles has been investigated. We observed that the modulation and velocity of laser have tremendously changed the diameter and spacings of the micro-circles formed on the photoresist. The ability to control the pattern formation on the photoresist has been confirmed in our study.

2. Experimental

Soda lime glass with 25×25 mm dimensions was used as substrate in this photoresist patterning study. The substrate was ultrasonically bathed in acetone for 5 minutes, in isopropyl alcohol for 5 minutes, and in deionized water for 10 minutes, respectively, followed by drying with nitrogen gas. A type of positive photoresist, named S1805, was coated onto the clean glass before the patterning process. The photoresist coating was carried out by spin coating at 4000 rpm for 40 seconds. It was confirmed by optical microscopy and profilometer measurements that the photoresist has a smooth surface with approximately 500 nm thickness.

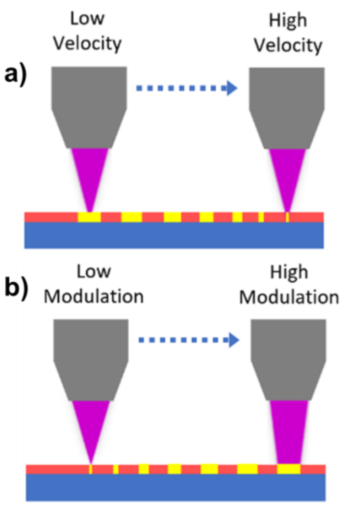

Fig. 1. The sharpness of the laser tip under low and high velocity at constant modulation (a), under low and high modulation at constant velocity (b) (color online)

The pattern made up of squarely packed micro-sized circles was defined and transferred onto the photoresist via Kloe Dilase 650, a maskless direct laser writer system. The laser at 375 nm wavelength shined on the photoresist to carry out the laser scribing. During the laser writing of micro-circles, the "contour" and “filling” parameters were applied to identify the outlines and to fill the outlines of the circles, respectively. While fine laser writing is required for contour formation, a thicker laser is used to achieve the filling. For this reason, low modulation and high velocity conditions should be applied for the contouring process. On the other hand, high modulation and low velocity would be necessary to successfully fill in the circles. The thickness of the laser tip and its signature on the photoresist according to different velocity and modulation values are schematically demonstrated in Fig. 1.

The modulation is the percentage of laser energy, and the writing speed is the laser line scribed onto the photoresist per second. Thus, the modulation and velocity should be tuned accordingly to find the proper conditions for both contour and filling since the laser conditions directly affect the pattern formation. Specifically, the diameter of the circles and thus the spacing between them strongly depends on the laser tip sharpness applied during the contour and filling formation process. The modulation and velocity of laser used for the contour and filling of circles are summarized in Table 1.

Table 1. Modulation and velocity values used in the laser writing of contour and filling of micro-circles

Modulation (% E)		Velocity (mm/s)	
Contour	**Filling**	**Contour**	**Filling**
10	50	0.1	1
5	25	0.4	4
2.5	12.5	0.7	7
1.25	6.25	1	10

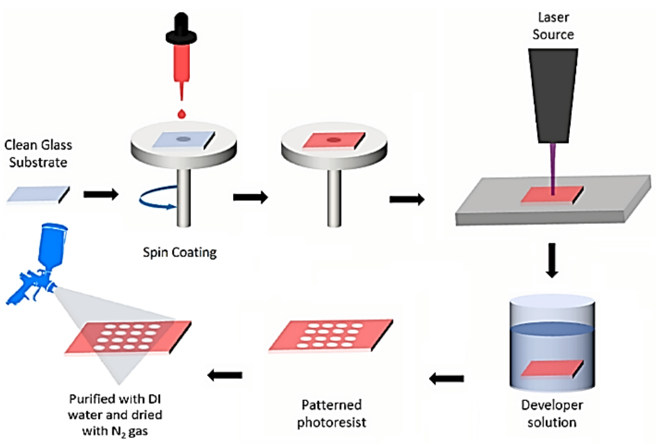

Fig. 2. The steps of the photoresist patterning process; the photoresist coating onto the clean substrate, the laser writing of desired pattern onto the photoresist, and the developing process to obtain the micro-circles (color online)

A specific developer solution called MF319 for positive photoresist was used in developing process. After development, the substrate was cleaned with deionized water and dried with nitrogen gas to remove the developer residues that could remain on the substrate. The whole photoresist patterning process is shown in Fig. 2. Thus, we could obtain micro-holes at the end of the patterning process. The real images of micro-holes were captured by optical microscopy (Reinshaw Raman-SPM/AFM). The 3D image and depth profile of the micro-holes were investigated via profilometer (Bruker Dektak XT Profilometer).

3. Results and discussion

The optical images of micro-holes whose contours and fillings were obtained under different laser modulation and velocity values are demonstrated in Fig. 3. The micro-holes start to show up from the one whole integrated structure and move away from each other by increased velocity at each modulation. Indeed, this tendency becomes more significant for lower modulations. Specifically, micro-holes with the lowest diameter and highest spacing are obtained when the highest velocity and lowest modulation are applied. Thus, it can be interpreted from the images that it is possible to control the physical parameters of micro-holes with the nearly perfect spherical shape by properly tuning the modulation and velocity.

The diameter of the circles and spacing between them in the lateral direction are schematically demonstrated in Fig. 4a. The degree of the change in physical parameters of micro-holes can be expressed numerically by the ratio of spacing between the circular holes to their diameters, as shown in Fig. 4b. Only the spacing to diameter (s/d) ratios of the patterns at the top-left to bottom-right diagonal of Fig. 3 are included in Fig. 4b since the change in formation of the circles can be seen more clearly in this diagonal axis. The s/d ratio belonging to the first pattern (V0-M0) cannot be calculated as the formation of micro-holes could not end up. The s/d is drastically increased from the starting (V1-M1) to the ending (V3-M3) pattern. Precisely, the s/d ratio of (V3-M3) pattern is approximately 18 times bigger than the first pattern (V1-M1). The increment of s/d ratio in Fig. 4b is more apparent (~ 7 times) from V1-M1 to V2-M2, while the lower s/d ratio (~ 3 times) can be seen from V2-M2 to V3-M3.

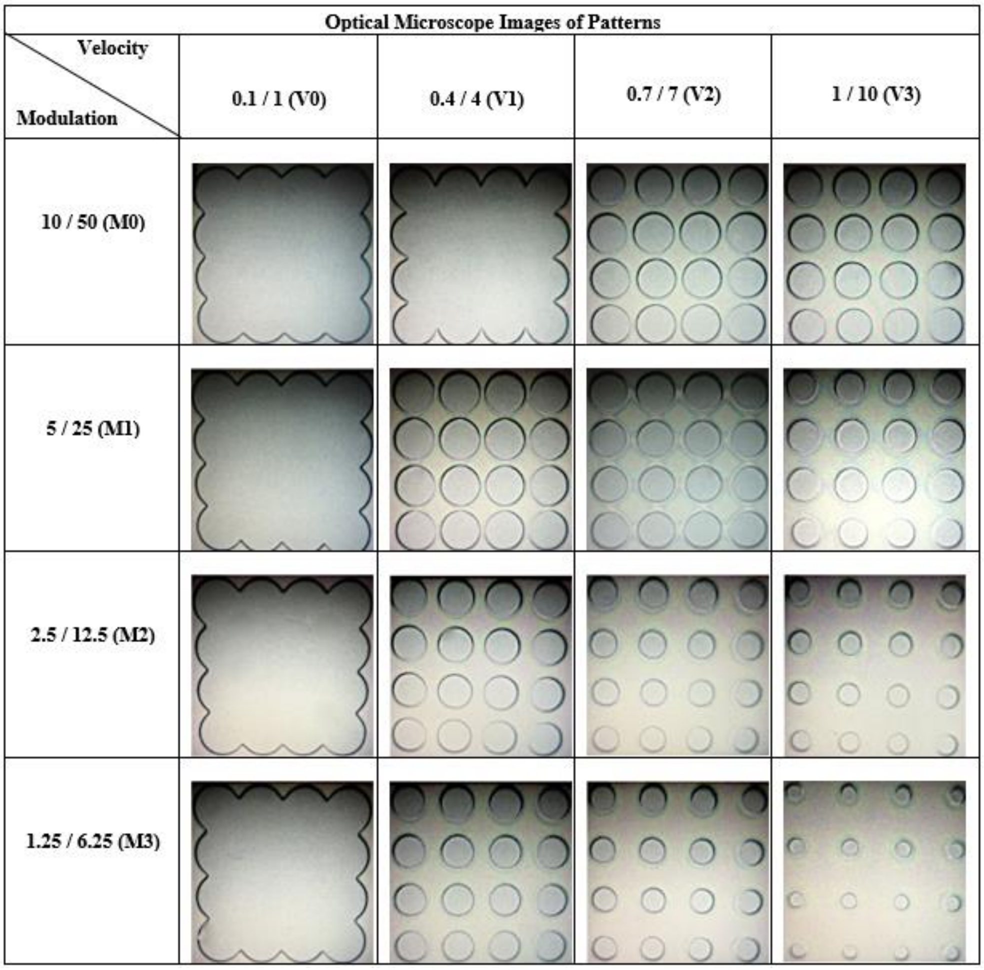

Fig. 3. Optical microscope images of patterns on the photoresist obtained at different modulation and velocities

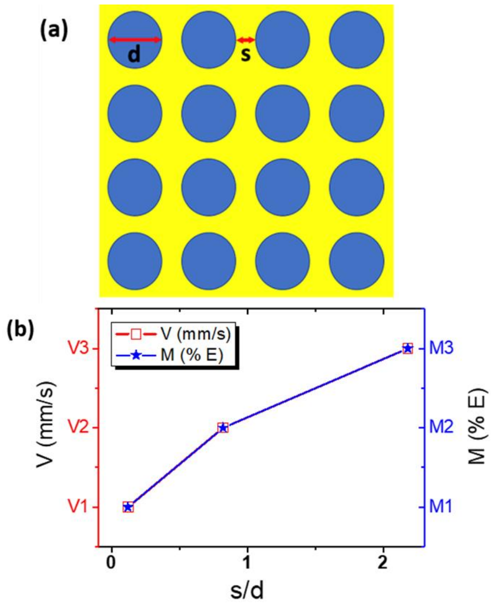

Fig. 4. Schematic demonstration of diameter and spacing of micro-holes (a), and spacing to diameter ratio dependence on the velocity and modulation (b) (color online)

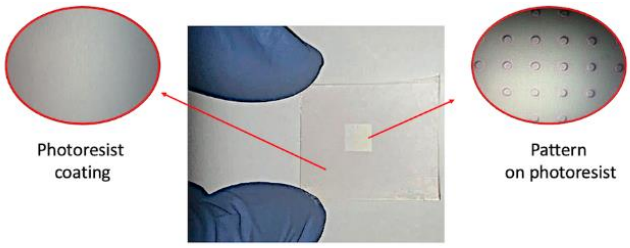

Fig. 5. The photo of glass substrate with photoresist coating and pattern formation (middle), enlarged image of the photoresist (left) and micro-holes (right) (color online)

Although we have not crossed a study that directly investigates the effect of laser parameters onto the diameter and spacing of micro-circled structures patterned on photoresist, there are few other reports that the micro-circle size (diameter) increases by enhanced laser power and exposure time that supports our findings [22, 23]. Table 2 summarizes the size-dependence of micro/nano-structures by applied laser parameters.

Table 2. The size-dependence of micro/nano-structures on the applied laser properties

Laser Parameters		Micro/Nano-structure size
Energy (Modulation)	**Exposure Time**	
63-133 (mJ/cm^2)	18 - 38 s	3.9 - 5.7 µm [22]
NA	0.4 - 0.5 s	29 - 30 µm [23]
4.8 - 4.3 mW	NA	1.528 -1.519 µm [24]
2 - 10 µW	NA	~ 200 - 500 nm [25]

The real image of glass substrate with smooth and homogenous photoresist coating and micro-holes on photoresist is shown in Fig. 5. The patterned photoresist with micro-circles can be seen even by the naked eye as the colour change is apparent (middle image). This case is typically observed in the patterned glass studies [26]. The homogeneity and smooth surface formation of photoresist are demonstrated on the left image while the micro-holes can be seen on the right. The organized and well-defined formation of micro-holes defined on the homogenous photoresist is evidence of a successful process.

The 3D image of pattern with the highest spacing-to-diameter ratio obtained by V3-M3 parameters can be seen in Fig. 6a. The red line drawn on the pattern represents the scanning direction of profilometer’s stylus. Since the positive lithography process was the subject of this study [27, 28], the photoresist has been etched down and micro-holes with 10 µm (± 11 %) diameter has been obtained as a result. The spacing between micro-holes can be evaluated as 15 µm (± 10 %) at the spot close to bottom and 30 µm (± 8 %) on the top parts of the structures from depth profile. Thus, the s/d ratio can be concluded in the range of 1.5-3.0 from the bottom to the top which is consistent with previous interpretations. The holes have fine circular shapes with approximately 500 nm depth which is the thickness of the photoresist, concluded from Fig. 6b. The depth profile of the pattern was recorded through the red line as demonstrated in Fig. 6a.

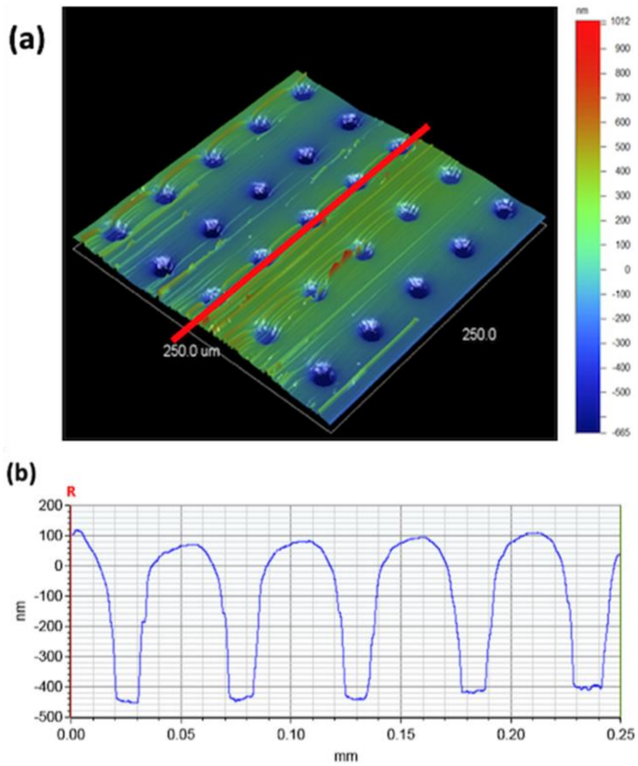

Fig. 6. The 3D image of the micro-holes (a), and the depth profile of the holes (b) (color online)

4. Summary

In conclusion, the positive photoresist coating and patterning via maskless photolithography has been performed in this study. It was found that the velocity, laser writing speed, is more effective at low modulations on the formation of micro-holes with lower diameters and higher spacings. While, modulation is more effective at higher speeds. For instance, the micro-holes become visible at the beginning and tend to separate further from each other as giving an s/d ratio of ~7 and ~3, respectively, for V2-M2 and V1-M1 patterns by the increment in speed and decrement in modulation. Indeed, the separation becomes more apparent as the 18-fold in s/d ratio is obtained from the comparison of the last pattern (V3-M3) to the first one (V1-M1). Furthermore, it was confirmed by depth profile measurement that well defined and separated micro-holes with 500 nm thickness and 10 µm diameter (V3-M3) could be successfully obtained, although the diameter varies for each pattern. In conclusion, we have revealed in this study that the physical dimensions of micro-holes can be precisely controlled by tuning the laser parameters accordingly, yet an effective and practical way of preparing a positive photoresist mask was introduced.

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