

Grayscale photolithography with phase change material photomasks

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Abstract—Here we report a grayscale photolithography technique using phase change materials, by inducing a multi-level refractive-index-changing phase-transition with femtosecond pulses. The grayscale phase change materials are used as the photomasks to locally change the exposure dose to enable shaping photoresist contour and developing 3D silicon structures. Unlike traditional photomasks, the transmission efficiency of phase change material masks can be tailored to arbitrary grayscale levels with submicron lateral resolution, and the spatial pattern can be optically reconfigured on demand.

Grayscale photolithography, Phase change materials, Reconfigurable, Submicron resolution

I. INTRODUCTION

Photolithography is a process in micro/nano-fabrication used light to transfer geometric patterns from a mask to the substrate. A photomask plays a critical role in the lithography process. It is typically an opaque plate with holes or transparencies that allow light to shine through in a defined pattern [1]. In order to fabricate three-dimensional (3D) structures, a set of photomasks, each defining a pattern layer are individually selected for exposure within multiple photolithography and alignment process cycles, typically up to several tens times, which is both time consuming and technically challenging. In light of this, grayscale lithography mask is a very attractive proposition, allowing fast-turnaround, 3D microdevice prototyping.

In the past few years, there have been many advances in grayscale mask design and lithography process. A state of the art halftone grayscale mask consists of opaque chrome spots and transparent clear spots in the chrome film coating on the glass substrate [2]. Since the transmittance of a gray level is determined by the ratio of the number of two kinds of spots, the lateral resolution element can reach at micron scale. Other kinds of halftone grayscale masks include the grayscale patterns in a photo-emulsion film or a photographic emulsion glass plate by varying the number density of the silver grains to get the micron lateral resolution as well [3]. HEBS-glass photomask has a continuous tone of gray levels to produce submicron patterns in each lateral dimension using nano-silver-

particle in the glass [4]. However, the requirements of electron beam exposure and high fabrication cost restrict their applications to a limited range of shapes, and not scalable to large-scale processing. In this paper, a novel reconfigurable grayscale photomask based on nanoscale phase change film is reported with submicron spatial resolution.

The photomask is prepared on the Ge₂Sb₂Te₅ (GST) film for writing grayscale patterns. Due to the extremely huge optical property change between the amorphous and crystallization states in GST film, the grayscale pattern is formed with controlled femtosecond (fs) pulse energy and pulse number for gradual crystallization of material [5, 6]. Ovonic nature of the phase change in GST film provides much flexibility to erase and rewrite the patterns to correct the errors and to be repeatedly used in batch production. The grayscale pattern in the mask is transferred onto Si wafer with a one-step photolithography process, followed by a reactive ion etching process to create multi-depth of pattern, thus enabling patch manufacture for widespread adoption.

II. EXPERIMENTAL RESULTS

In our experiments, a three-layer phase-change thin film, composing of an amorphous GST layer of 70 nm thickness sandwiched between two 70 nm protective layers of ZnS-SiO₂, is prepared by sputtering deposition on to a silica substrate. The 730 nm fs pulse trains are reduced to 1 MHz frequency and highly focused on GST film to write and re-write submicron scale marks (typically 0.6 μm) as the grayscale pattern. As fs laser pulse trains with lower pulse energy (~0.39 nJ) are applied, the optical canvas is heated below the melting point but above the glass-transition temperature and gradually crystallized. The transparency of the crystallized mark can be precisely controlled by changing the numbers of pulse and pulse energy applied on the canvas. Whereas, as a single high energy fs pulse (~1.25 nJ) applied, the GST mark is melted and quickly cooled, switching to amorphous phase state. With fs laser pulse induced ovonic (gradually) switch between amorphous and crystallization states, grayscale patterns are written, erased and re-written into a film of phase change material as the photomask with submicron resolutions. Using

the mechanism described above, reconfigurable binary or grayscale GST photomasks can be used for photolithography. As a demonstration, the grayscale lithography mask for the fabrication of 3D spiral phase plate (SPP) on Si wafer is prepared. SPP is a kind of beam mode convertor introducing a spiral phase into the passing wavefront. It has a thickness varies spiral staircase circumferally but uniform radially around the plate, normally fabricated by multi-step photolithography and etching [7].

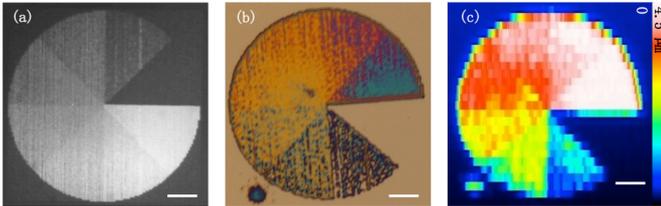


Figure 1 a. The reflection microscope image of 8 level gray scale pattern written in a GST thin film. b. The color image of 3D photoresist structure left on Si wafer after photolithography and photoresist development. c. Surface profiler characterization of 3D SPP pattern with each section has different thickness. Scale bar: 10 μm .

Figure 1a shows the optical image of the grayscale GST photomask prepared by fs pulse numbers varying from 0 to 80. It composed of 8 grayscale levels patterns along clockwise, which change the exposure dose locally to make differential depth of exposed photoresist across the surface. The GST photomask is purposely stucked onto the blank mask as the grayscale photomask when used in maskalign machine (Karl Suss Mask Aligner-MA6, intensity $19\text{mW}/\text{cm}^2$, 120s) so as to transfer the pattern on the spin-coated photoresist (AZ1505, 6000rpm, $1\ \mu\text{m}$). After 120s i-line broadband illumination and 1 minute's dipping in the developer, a photoresist pattern with various thicknesses is obtained on the Si wafer substrate as the etching mask, as shown in Fig 1b. The color of pattern is coming from interference of light between top and bottom of photoresist. After the dry plasma etching (Oxford Plasmalab 80 plus), the photoresist is depleted leaving the desired 3D pattern standing on the Si wafer. Figure 1 c demonstrates the surface profiler imaging of 3D SPP pattern in Si substrate. Along clockwise, the sections of SPP have gradually increased height from 0 to $4.5\ \mu\text{m}$.

The exposure time is one of key parameters to benchmark the lithography process. Due to low UV transmission of GST in amorphous state compared to standard mask substrate, long exposure time is necessary and need to be optimized in

grayscale lithography process. However, compared to multi-alignment for grayscale lithography with binary photomask, our proposed grayscale GST photomask method is one step lithography with low cost and non-accumulative alignment error.

III. CONCLUSIONS

Here we report reconfigurable, submicron resolution grayscale photography mask based on nanoscale phase change thin film. The grayscale mask is prepared by optically directly writing patterns on the GST with fs pulse trains of controlled pulse energy and pulse number for gradually crystallization of material. A spiral shaped 8-level Si pattern is fabricated in one lithographic step with GST grayscale mask. With this optical directly writing grayscale GST photomask technique, arbitrary 3D structures are possible to be fabricated with one-step optical lithography, which will pave the way to widely applications in fabrication of diffractive optical elements, blazed gratings, integrated photonics circuits and MEMS system.

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REFERENCES

- [1] M. J. Madou, *Fundamentals of Microfabrication* (CRC, Boca Raton, FL) (1997).
- [2] U.S. Patent 2004/0009413 A1 (15 Jan 2004) T. E. Lizotte.
- [3] Reilly, James M. *Care and Identification of 19th-Century Photographic Prints*. Eastman Kodak, Rochester, NY: 1986.
- [4] L. A. Wu C.-K. Wu, U.S. patent 2003/6562523 B1 (13 May 2003).
- [5] Q. Wang, J. Maddock, E. T. F. Rogers, T. Roy, C. Craig, K. F. Macdonald, D. W. Hewak, and N. I. Zheludev, *Appl. Phys. Lett.* **104**, 121105 (2014).
- [6] Q. Wang, E. T. F. Rogers, B. Gholipour, C.-M. Wang, G. H. Yuan, J. H. Teng, and N. I. Zheludev, *Nat. Photonics* **10**, 60 (2016).
- [7] S. S. Oemrawsingh, J. A. van Houwelingen, E. R. Eliel, J. P. Woerdman, E. J. Versteegen, J. G. Kloosterboer, and G. W. Hooft, *Appl. Opt.* **43** (3), 688 (2004).