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Laser-induced grayscale patterning in TeO_x thin films

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ABSTRACT

Grayscale patterns have been widely studied and applied in many fields. In this paper, grayscale patterns with precise grayscale changes are fabricated on TeO_x thin film by laser pulse with respective wavelengths of 635 and 405 nm. Two obvious changes according to the different grayscale level emerge as laser energy increases. The first change is from invisible to white-grayscale with low laser pulse width between 2 ns and 50 ns. After a transient period with laser pulse width between 48 ns and 55 ns, the grayscale in the second change becomes darker and darker following the laser pulse width increases from 56 ns to 250 ns. The mechanism of the grayscale change is partly explained and verified by TEM, which involves the agglomeration and segregation of Te, crystallization and recrystallization after melting of Te and TeO_2, and ablation of TeO_x, wherein different mechanism is dominant in each stage. We can obtain grayscale patterns with precise grayscale changes to meet specific requirements by controlling the parameters precisely.

1. Introduction

Grayscale patterns usually appear visible change from bright to dark under microscope due to obvious differences in optical density (OD) or transparency, and have been widely studied and applied in optical, mechanical, fluidic, and micro-electro-mechanical systems (MEMS) [1–6]. Generally speaking, grayscale patterns are continuous or multilevel surface micro- or nanostructures on the sample surface. Various fabrication techniques have been reported to create surface gradient height structures, such as photo-induced lithography [7], electron-beam lithography [8], and focused ion beam lithography [9]. However, many of these techniques either require unconventional and costly process equipment, or are not suitable for repeatable batch fabrication [2]. Furthermore, the grayscale patterns are usually fabricated on photoresist by beams with special intensity in these grayscale lithography techniques, but the resist is usually covered by a mask [10,11], in which the template patterns have been pre-fabricated. Many masks have been created on chalcogenide glass [8], chrome [12], and polymer [13]. In lithography process, the amount of retained resists after undergoing exposure and development processes is according to the grayscale level of the mask [12]. Given the difference of exposure intensity on the resist after the mask, the 3-dimensional patterns with gradual height profile could be obtained after the remaining resist has been developed and etched. Nowadays, large-area patterns with gradient profiles have been fabricated successfully by grayscale lithography using photoresist; this plays an important part in further transferring the patterns to the silicon substrate with reactive ion etching (RIE) technology [8,14]. However, photoresist is only sensitive to a certain laser wavelength. Furthermore, it also needs further developing and etching procedures, resulting in increased processing time and cost.

Tellurium suboxide (TeO_x) [15,16], one of the chalcogenide phase change material [17,18], has been extensively investigated and used in both scientific and industrial applications, such as digital laser recording media [15,19], due to its excellent storage ability, high sensitivity and resolution, and low fabrication cost. The as-deposited TeO_x film in vacuum actually consists of Te metal micrograins usually with diameters that are less than 2 nm and embedded in an amorphous TeO_2 matrix of a special granular structure [20–23]. The recording mechanism has been explained by two theories: one is the phase transformation of Te grains from amorphous to crystalline [24–27], and the other is the segregation of Te particles to the near surface [20,21]. Regardless of the actual reasons behind the change in optical behaviors of the TeO_x film, the result indicates a visible change from bright to dark under laser pulse irradiation. And according to systemic experiments, we found

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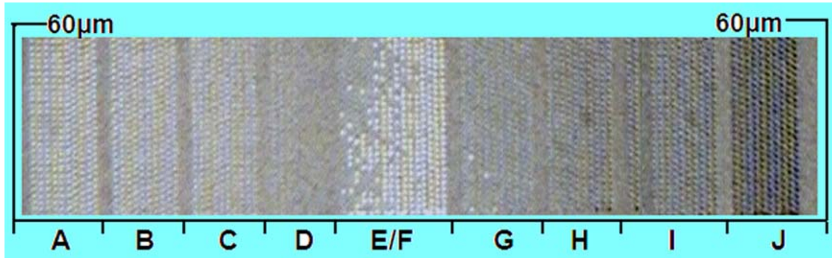

Fig. 1. Reflection OM photos of the gradual change process of grayscale patterns induced by laser pulse on TeO_x film.

that we can further obtain more precise color change under optical microscope by adjusting the laser parameters.

In this paper, we used laser pulse to fabricate the grayscale patterns directly in the TeO_x thin film. Compared with the photoresists, the TeO_x thin film has many advantages as follows: first, it is not sensitive to laser wavelength, that is, different wavelength lasers could be used as the exposing light source in this materials; second, grayscale change occurs in a low laser power and does not need any mask layers; third, this material does not require further developing and etching processes that could decrease time and cost. Most importantly, it has good potential to achieve higher spatial resolution with high throughput. In the end, the mechanism of the grayscale change is partly explained and verified by TEM, which involves agglomeration and segregation of Te, crystallization and recrystallization after melting of Te and TeO_2, and ablation of TeO_x. In addition, different mechanism is dominant in different stages. We can obtain grayscale patterns with precise grayscale changes to meet a specific requirement by controlling the parameters precisely. We hope that this technology will be applied to scientific and industrial fields.

2. Experimental detail

Single-layered TeO_x film was prepared on K9 glass using the radio frequency (RF) reactive magnetron-control sputtering method when a pure Te target with a diameter of 60 cm was bombarded by a gas mixture of Ar/O_2 plasma at room temperature. The background pressure was approximately 1.5×10^{-4} Pa, and the sputtering pressure was about 0.8 Pa of Ar/O_2 environments; the RF power was 40 W. By controlling the oxygen flow ratios of $O_2/(O_2 + Ar)$ and systemic checking experiments, the TeO_x film with thickness of 100 nm was then prepared according to the optimized oxygen flow ratios of 0.1. The red laser writing system (λ = 635 nm, NA = 0.9) was used to fabricate spot-shape patterns, and laser power was fixed at 5.0 mW, meanwhile pulse widths were adjusted from 2 ns to 250 ns. The blue laser writing system (λ = 405 nm, NA = 0.9, continuous light mode) was used to fabricate 'SIOM' letters pattern, and laser power was adjusted between 2.5 mW and 8.0 mW. Finally, the grayscale patterns induced by laser pulse were observed by optical microscope (OM) and scanning electron microscope (SEM, FEI, SIRION 200). The mechanism of different grayscale levels were qualitatively analyzed by transmission electron microscope (TEM, JEM-2010), and the film was sputtered on copper grid and irradiated by the same red laser writing system with NA of 0.25 for investigation easily.

3. Experimental results

Fig. 1 is the reflection OM photo and presents the gradual change process of grayscale induced by laser pulse in TeO_x film. We can see clearly the grayscale level changes from light-gray to white and then to black following the laser energy increases. In order to observe the patterns in detail, the SEM pictures were done. Fig. 2 shows the SEM pictures of the grayscale patterns with different shapes fabricated in TeO_x film induced by red laser pulse, and the insets are the corresponding reflection OM photos appearing different grayscales with the corresponding pulse width listed in the bottom of every photo. The laser power is fixed at 5.0 mW; meanwhile, the pulse width is ranged from 2 ns to 250 ns. As shown in the OM photos, we can clearly see the gradual color change from white to black following the laser pulse width increases, and different grayscale corresponds to different morphology in SEM pictures. The grayscale patterns can be divided into three regimes according to the different grayscale levels, denoted by I, II and III, respectively.

Regime I: The patterns, including parts (a), (b), (c), and (d), appear as light-gray spots on a dark-gray background in the OM photos, and are induced by lower laser energy with only several nanoseconds of pulse width between 2 ns and 50 ns. It is obvious to see in OM photos that the color in regime I become thinner and fainter until become invisible as the laser energy decreases. Furthermore, the sizes of the spots in this regime also become much smaller when the laser pulse width is only several nanoseconds. From the SEM pictures, we can clearly see the spot size gradually decreases from 1.5 μm in Fig. 2(a) to only about 200 nm in Fig. 2(d) with little spot traces on the film. When we further decrease the laser energy, we almost cannot see the pattern, which appears almost the same as the TeO_x film. It is noted in the SEM pictures that the obvious difference in morphology is clearly observed, which could be the result of the agglomeration and segregation of Te particles and the crystallization and recrystallization after melting of Te grains, which could be discussed in the next section.

Regime II: As the laser energy increases, the color also changes from light-gray to white, and the obvious change occurs in regime II, which includes parts (e) and (f) and the pulse width is from 48 to 55 ns. Fig. 2(e) and (f) represent two kinds of patterns with different morphology, just as shown in SEM picture. From the OM photos, we can see Fig. 2(e) looks similar to the patterns in regime I with light-gray spots on a dark-gray background and like a dimple-bowl shape, moreover, the color in Fig. 2(e) is near pure white and demonstrates the best optical contrast between the irradiated area and the as-deposited film. Whereas Fig. 2(f) looks different from Fig. 2(e) and the patterns appear as a white ring surrounding the black center. The further obvious observation is applied by SEM pictures. It is shown in the SEM picture that two kinds of patterns with different morphology emerge; the patterns in Fig. 2(e) looks similar to the patterns in regime I, and the patterns in Fig. 2(f) appears as a deep hole in the center of the spot. Furthermore, the two kinds of patterns are mixed together and the quantity of the patterns with deep holes increases as the laser energy increases. So we can know that this situation corresponds to the threshold effect of the TeO_x material. When the laser energy increases beyond the certain value, the patterns will transform into Fig. 2(f) from Fig. 2(e), and we can call this regime the 'transition zone'. From the OM photos, we can obtain the pulse width for this threshold effect is about 50 ns.

Regime III: The patterns in regime III include parts (g), (h), (i), and (j) show the best optical contrast between the irradiated area