

Research Article

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Direct Patterning with Femtosecond Laser for Fabricating Ge2Sb2Te5 Stamps and Imprinting of UV Resins

Lin CB1*, Cheng PY1 and Lin HY2

¹Department of Mechanical and Electromechanical Engineering, TamKang University, Tamsui, Taipei, Taiwan, R.O.C ²Mechanical Industry Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan, R.O.C

Abstract

A novel method to fabricate a micro-scaled meter metallic stamp for imprinting is proposed in this study. Phase transformation film of amorphous Ge2Sb2Te5 (GST) was first deposited on cleaned silicon substrates by using DC sputtering process. The GST film is then irradiated with the femtosecond laser pulse directly through the photomask to photomelt and induces 2D-crystalline marks formed on the original amorphous region. Owing to the varied chemical properties between the amorphous region and crystalline marks, the crystalline marks were etched by using nitric acid mixed with ethanol. It is with this method that a micro-scaled meter metallic stamp was fabricated. Furthermore, the SU-8 polymeric patterns were successfully replicated and easily demolded from the etched GST stamp by using imprinting. Ultimately, with imprinting, the etched GST stamp could successfully replicate and also easily demold the SU-8 polymeric patterns.

Keywords: Phase transformation; Femtosecond Laser; Photomelting; Etching; Imprinting

Introduction

Imprinting technology is one of the most promising technological inventions characterized by low-cost, high fidelity, excellent repeatability and mass-production of micro or nanoscaled meter patterns over large areas while employing a single lithographic step [1-6]. The process has been used for fabricating micro or nano scaled meter patterns and devices in various fields, such as magnetic data storage, biotechnology, optics, electronics, single electron transistors and subwavelength optical elements. The key to successful imprinting technology is the use of the patterns in micro or nanoscaled meters, the replication of high resolution in large areas and the avoidance of adhering the polymer to the stamp. The direct electron beam lithography (EBL) combined with conventional dry ion etching and metal lift-off process is a powerful tool in imprinting lithography metallic stamp production [7]. However, using the EBL process to fabricate a large area of imprinting metallic stamp is expensive because of the long processing time: Hence, a novel imprinting lithographic metallic stamp is proposed as a new solution in this study, which the metallic stamps is materialized at a low cost with a low aspect ratio. The solution is made possible by using phase transformation films, femtosecond laser irradiation and etching process.

Femtosecond laser technology has been employed in a wide range of applications in many fields, such as machining and the production of optical components. Recently, a large number of femtosecond ablation studies were carried out, investigating materials including polymers, ceramics, metals and semiconductors. The main characteristics of femtosecond-pulse laser ablation are (i) having very rapid heating rate; (ii) leaving no molten materials; and (iii) being able to operate within a very small the heat-affected zone. According to Shen [8], by using ablation and the femtosecond laser the surface of the workpiece and rapid heating rate-can be used to fabricate micron-scaled meter patterns. In addition, according to Frank [9], a two-dimensional nanoscaled meter pattern is performed by direct-write femtosecond laser ablation a femtosecond laser direct ablative writing technology. Li [10] use a femtosecond laser to produce an optical element. According to Pronko [11], they have ablated holes, by laser ablation, into a metal film. Using 200 fs, 800 nm pulses from a Ti:sapphire laser, focused to a spot size of 3000 nm, we have produced holes with a diameter of 300 nm and a depth of 52 nm. According to Leitz [12], short pulsed micro- and nanosecond systems generally allow high ablation rates. Yet, thermal damage of the workpiece cannot be avoided completely. Ultrafast pico and femtosecond systems allow a higher precision, yet at lower ablation efficiency.

Phase-change materials can be changed from a non-crystalline phase to a crystalline phase both reversibly and non-reversibly, and the materials have been applied to different industry uses, such as data recording and storage. There are three different forms for phasechange material: (1) the crystalline phase is converted irreversibly into the non-crystalline phase such as Sb₂Se₂/Bi₂Te₂; (2) the non-crystalline phase is converted reversibly into the crystalline phase such as Ge,-Sb₂-Te₂ (GST); (3) the crystalline phase is converted into another crystalline phase such as In-Sb-Te. This study chooses GST as phase change material because the GST materials have high crystallization speed and thermal-stability [13]. According to Yamada [14], using an 830 nm laser irradiation wavelength and 8 mW energy on the different chemical compositions of GST can result in different crystallization time. Meanwhile, based on Yamada et al.'s observation, GST has two crystalline phases: one is meta-stable phase (face-centered cubic crystal structure), and the other is stable phase (hexagonal crystal structure).

Figure 1 illustrates a newly fabrication method using metallic stamps for imprinting Ge_2 -Sb₂-Te₅ (GST) amorphous film was firstly irradiated by using the femtosecond laser and photomelting to induce phase transformations and then the formation of crystalline mark on the amorphous film. By using the chemical properties, the amorphous

*Corresponding author: Lin CB, Department of Mechanical and Electro-Mechanical Engineering, Tamkang University, Tamsui, Taipei, Republic of China, Tel: 886-02-26215656; E-mail: cblin@mail.tku.edu.tw

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and polymeric microstructure replication by a UV-crosslinkable resins.

area and the crystalline mark were varied, and then the crystalline mark was etched to make an imprinting metallic stamp. Finally, with these imprinting techniques, a polymeric structure is replicated.

Experiment Procedure

GST Film preparation

Firstly, the 4 inch silicon wafer as a substrate was cleaned by a dionized water (DI), followed by an RCA cleaning and DI rinsing process, and subsequently rinsed with an HF dip and DI and dried by nitrogen. Then, the Ge₂-Sb₂-Te₅ (GST) films were deposited on the cleaned silicon substrate by using DC sputtering process at room temperature. The parameters of DC sputtering were enumerated as follows: the base pressure of the chamber was 8×10⁻⁶ torr, Ar work pressure of 5×10-3 torr, the growth rate, as a result, was about 0.45 nm/s; the applied power of 100 W was used to deposit the GST films for 15 minutes, in which the as-deposited GST films were in amorphous state. The average composition of the as-deposited GST film was measured by the electron probe X-Ray micro-analyzer (EPMA), Next, to measure the thickness of the as-deposited GST amorphous film, a LEO-1530 scanning electron microscope is used to observe morphology. Meanwhile, a D3000 atomic force microscope (tapping mode) measured the surface roughness (Ra) using five different portions. Each sample of this measurement is shown in Figure 2, which the scan area at each portion is 2 um \times 2 um.

Photomelting induced phase transformation

The femtosecond laser system employed in this work consisted of a self-mode-locked Ti: sapphire laser and a 1 kHz chirped-pulse regenerative amplifier (CPA; spectra physics, spitfire,) as shown in Figure 2a. The output pulses of the Ti sapphire laser were selectively amplified in the CPA, producing femtosecond pulses of 1 mJ/pulse in energy and 120 fs in duration at a repetition rate of 1 kHz. Firstly,



Figure 2: Schematic diagram of (a) The femtosecond laser system; (b) Schematic diagram of the experimental setup for single-step fabrication using 1 KHz femtosecond laser, which (a)laser beam is focused using a lens and (b) without using a lens.

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optical neutral density filters were placed in the beam path to attenuate the pulse energy from 1 mJ/pulse down to 10 µJ/pulse. Then, the CPA output was split into two parts by a beam splitter. Optical neutral density filters were also used to control the pulse energy of 1-10 µJ/pulse onto the GST films. The irradiation time was controlled by switching an electrical shutter with a visual basic program. If the laser beam was focused using a lens in the light spot as shown in Figure 2b. Owing to the fact that the spot size D was $0.6 \lambda/NA$, wherein λ was the wavelength of incident light, NA is the numerical aperture of the wavelength. The wavelength and numerical aperture were 800 nm-and 0.4 respectively in this study. Therefore, the ideal spot size was 1.2 micron meter. In addition, the working distance of a focus on the specimen affects the spot size, so the actual size was about 50 to 80 micron meter. Due to the fact that each size of the photomask pattern area of the present study was 2 mm \times 2 mm, the pattern cannot be formed fully on the GST sample. In order to overcome the limit of the spot size, the laser beam is not focused by using a lens, but by using laser irradiation directly through photomask on the GST sample as shown in Figure 3. The laser beam spot melted the portion of the GST amorphous films directly through a photomask, and the crystalline mark was formed during rapid cooling process at the position where the cooling rate was faster than the threshold [15]. For precise positioning and scanning, the specimen was placed in precision x-y-z stage. The topography of irradiated GST samples was also examined by the optical microscopy (OM).

Metallic stamp fabrication

Because the chemical properties are difference between the amorphous region and the crystalline mark of irradiated GST film, and the crystalline mark can be etched by the adapted etching solution and conditions, three dimensional patterns could be generated on the GST film b. Two etching processes are described as follows: (1). An aqueous solution of 70% nitric acid (HNO₃) and DI water were mixed to prepare for the etchant with a volume ratio 1:5 at 25°C. Then the irradiated GST film was etched in the etchant for 1 minute. During etching process, the etchant was stirred continuously in a forced convection by using magnetic agitator at 8°C for 1 minute. In order to improve the surface roughness and the etching rate, the etchant was oscillated in the ultrasonic cleaner with ethanol for an hour to remove the etching products. Finally, the stamp was dried by nitrogen and then was



Figure 3: SEM morphology of the as-deposited GST film on the cleaned silicon substrate.

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	Chemical composition (at. %)		
	Ge	Sb	Те
Stoichiometric composition	22.2	22.2	55.6
Specimen no. 1	20.1	23.8	56.1
Specimen no. 2	19.9	24.1	56.0
Specimen no. 3	20.1	23.7	56.3
Specimen no. 4	20.2	23.8	56.0
Specimen no. 5	20.0	23.5	56.5
Average composition	20.1	23.8	56.2

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obtained. (2) In order to decrease the hydrogen over-potential, which in turns makes a low surface roughness of the GST stamp, a nitric acid was mixed with ethanol to prepare for the etchant with a volume ratio 2:5 at 25°C. The other etching process was the same as the condition mentioned in [1]. The morphology of the metallic stamp was observed by D3000 atomic force microscope in tapping mode.

Imprinting process

The SU-8 photoresist was spin-coated onto the surface of the GST stamp in three steps. Firstly, the spread cycle was ramped up to 500 rpm at 100 rpm/s acceleration in five seconds and then the spin cycle was ramped to final spin speed at an acceleration of 300 rpm/s and held at this speed for 30 seconds. Secondly, to volatilize the solvent in SU-8 photoresist, the stamp was pre-baked at 95°C on a hot plate for 2 minutes. Next, the coated GST stamp was cured and crosslinked in an UV oven for 2 minutes. Finally, the polymeric structures were demolded from the etched GST stamp and replicated successfully by imprinting technique. The morphology of replicated polymeric structure was observed by scanning electron microscopy.

Results and Discussion

Characteristic of the GST films

The thickness of the as-deposited GST film on the cleaned silicon substrate was around 400 nm, as shown in Figure 3. The average surface roughness (Ra) of GST film on the 4" silicone substrate in five different portions is around 0.9 nm. The average chemical compositions of the GST film with five samples determined by EPMA are summarized in Table 1, which was conducted with a slightly Ge-poorer and Sb-richer in the specimen than the stoichiometric composition analysis of the Ge₂Sb₂Te₃ alloy while Te stayed similar.

Crystalline marks induced by photomelting

1 mJ/pulse laser energy irradiated directly through photomask to the GST film and the photomask is contacted with the GST film. The GST film was produced by phase transformation that was conducted with the method of photomelting. Moreover, the induced original amorphous region was converted into a line arrayed with crystalline marks, and this process is called lithography. The size (w) and period (p) of lines arrayed with crystalline marks (w, p) was (2 μ m, 2 μ m) and (4 μ m, 4 μ m) respectively is shown in Figure 4. The active GST film went through a rapid and stable transformation from the amorphous region into a crystalline pattern after the irradiation process. What caused this transformation was that during crystallization process, the GST film was accompanied by exothermal and isothermal, and thus exothermic crystallization showed that crystallization included nucleation and grain growth.

Table 1: The chemical composition of the GST film at five different samples measured by EPMA analysis.



The crystallization time of the GST material was about 50 nanoseconds when the power of the femtosecond laser pulse was 8 mW [15], and the irradiation time of the femtosecond laser pulse was around 10⁻¹⁵s. Consequently, the thermal diffusion of the irradiation was limited in the ps order. Meanwhile, the entire energy content of the femtosecond laser pulse was absorbed locally, and the large thermal gradients thus established quickly and removed the heat from the irradiated spot. Owing to the efficiency of the shorter pulses (τ =120 fs) in this study in delivering the optical energy to the GST amorphous layer, the cooling rate was enhanced while the pulse-width was reduced. As was mentioned by Weidenhof [16], the thermal diffusivity in the amorphous phase is 1.3×10^{-7} m² / s, and that in the crystal phase was $4.7\times10^{\text{-7}}\,\text{m}^2\text{/s}.$ Therefore, the thermal diffusion length L within the GST amorphous layer was $(D\tau/c)^{1/2} \ll 1$ nm, in which D is thermal diffusion coefficient, τ was the width of pulse, the length was much smaller than both the thickness of the GST film and the focused spot's size, and this allowed the patterns to be formed accurately within the laser spot. We can see a different reflectance between the crystallization region and amorphous region, as shown in Figure 4. According to Weidenhof [14] definition, the relative change in reflectance ΔR between amorphous phase and crystalline phase is $(R_a - R_c)/R_a$, where R_a is reflectance in amorphous phase and R is reflectance in crystalline phase. The ΔR was above 8 % in the range from 400 nm to 700 nm [17], so that we can see obviously the contrast of reflectance between the crystalline mark and amorphous region. Therefore, when using laser irradiation with about 1 mJ/pulse energy directly through the photomask on the GST film and when contacting the photomask with the GST film, we can make a twodimensional rectangular array of crystalline regions, which formed the pattern is similar to the shape of the photomask, as shown in Figure 5.

The procedure is as stated above, regarding the direct irradiation of 10 mJ/pulse laser pulse energy through the photomask to the GST film and the result of the contact between photomask and the GST film. However, too much radiation energy caused material removal and generates the irregular forms of pits on the GST film, as shown in Figure 6. The penetration depth of the pulse laser and the ablation threshold can be used to determine whether the GST material is removed after being irradiated. What is more, the penetration depth consists of the light penetration depth and the heat penetration depth, the penetration depth of light is much smaller than 1/10 wavelength of the metal. For the 800 nm incident light in this study, the penetration depth is less than 80 nm, it can be ignored, so that the penetration depth is major from the heat penetration depth $l_{th} = 2\sqrt{\kappa \cdot \tau_H}$, where κ is the thermal diffusivity (in the crystal mark was 4.7×10^{-7} m²/s), τ_H is the pulse duration [18]. In consequence, the heat penetration depth was around 1.2 um in this study. For a Gaussian beam, the ablation area was determined by the ablation threshold and the energy density. Further, since the total energy of laser pulse 10 mJ/pulse is about 14 mW larger than ablation threshold, the GST material might be



Figure 5: (a) OM morphology of rectangle array generated by photomelting, which the white color is crystalline mark and the grey black is amorphous region.; (b) an original photomask.



Figure 6: (a) OM morphology of a spot arraySEM morphology of (b) a spot and (c) ripple under over irradiated GST film generated by photomelting, which the white color is crystalline mark and the grey black is amorphous region.

corroded and removed. Finally, a crater was formed on the surface in order to improve this shortcoming. The total energy of laser pulse must be reduced to below the ablation threshold and the heat penetration depth, while being able to produce a phase transformation.

Additionally, the spontaneous ripple structure was observed within the pit, as shown in Figure 6c. Because the modulation of interference produced between the incident and the reflected wave of the laser, the non-uniform energy was irradiated on the film. As Kautek [18], by using repeated femtosecond laser pulses to ablate an AlN target, the crater and ripple structure were also observed on the surface of target.

Three things are represented in Figures 7a-7d, a 1 mJ/pulse laser irradiation energy directly through the hexagon openings of the photomask on the GST film, the contact between the photomask and the GST film, and finally, the development of the crystalline marks with the hexagonal array generated by photomelting. At first, crystalline marks formed on the corner in a hexagon array as shown in Figure 7a, and then in Figures 7b and 7c, the six edges gradually formed and increased with laser irradiation. This is caused by the procedure that the corner would be produced with laser energy superposition; therefore, the energy at the corner can firstly reach the required energy



Figure 7: (a)-(c) OM morphology of hexagon array forming process generated by photomelting, which the whitecolor is crystalline mark and the grey black is amorphous region; (d) an original mask.



Figure 8: OM morphology of (a) the hexagonal array and (c) the round array with diffraction patterns generatedby photomelting, which the white color is crystalline mark and the grey black is amorphous region; (b) an original photomask of the round array; (d) an original photomask of the hexagonal array.

for crystallization threshold, that is, the crystalline mark was formed firstly at the corner.

Another procedure of inducing the crystalline mark via the use of photomelting is as following: 1 mJ/pulse laser pulse energy irradiated directly through the photomask to the GST film and the photomask does not have any contact with the GST film. The crystalline mark, accompanied with the diffraction patterns were formed simultaneously. While it was being formed, a crystalline mark was the constructive interference, and the diffraction patterns intersected with each other as shown in Figure 8. The reason for this was that the photomask did not contact with the GST film, a plane wave incident through the round or hexagonal slit of the photomask, due to each incident ray has same path difference. If the path difference was $\lambda/2$, then there would be bright and dark diffraction patterns, in which λ was the wavelength of incident ray.

GST stamps

The chemical properties of the amorphous area and the crystalline mark were varied, the crystalline mark can be etched by using adapted etching solution and conditions, three dimensional structures can be generated by adapting the etching process. The etched structure in which HNO₃: DI water (Vf% 1:5) etching solution functions is shown in Figure 9a. The crystalline marks were observed to be etched down to form the trench at the bottom, and their shapes were unequal to each other and near V type. Moreover, the morphology of the stamp in a rectangle array was very rough. This was because of the effect of hydrogen overpotential and the difficulty of removing the etching product at the bottom of the trench. Moreover, the fact that the etching solution flowed randomly and its static etchant of the amorphous area created an incomplete shape and a rough surface.

Comparatively, the etched structure within which HNO_3 : ethanol(Vf% 2:5) etching solution works is exhibited in Figure 9b. The side wall of the stamp compared with that in Figure 9a was found to be fairly vertical and deep. The major reason for this effect is that ethanol reduced hydrogen overpotential effectively and also lowered surface roughness to less than Ra 5 nm, surface roughness could be found both on the surface and at the bottom of the trench by the AFM cross sectional view.

Polymeric structure replicated by imprinting

Figure 10 shows that the polymeric structures were replicated by imprinting with the etched GST stamp. Due to SU-8 resins' high sensitivity, high resolution, fairly good adhesion, fluidity, and finally their high applicability on high-aspect-ratio structures, the SU-8 resins easily filled into the etched GST stamp. After the above-mentioned process, UV exposure can be easily demolded by the etched GST stamp to obtain the polymeric structure. It is worth-mentioning that it was found the bonding strength between the etched GST stamp and SU-8 resins to be smaller than the demolding stress. As a result, some polymeric structures could be easily carried out and de-molded by the etched GST stamp during replication.

Conclusion

The purpose of this study is to propose a new method of fabrication employing metallic stamps for imprinting micro scaled meter pattern. The Ge_2 -Sb₂-Te₅ (GST) amorphous film was firstly irradiated by using femtosecond laser directly through the photomask and by photomelting to induce phase transformations, and subsequently the crystalline marks were formed on the amorphous film. By using the



Figure 9: AFM 3D profile of the etched GST stamp with a line array etched by (a) DI water mixed etchant and (b) nitric acid mixed etchant.



chemical properties between the crystalline and the amorphous region was varied and crystalline area is difference, which the crystalline mark can be etched by using etching process. Further, the GST stamp with three dimensional structures was generated by adapting the etching solution and conditions. Finally, by using imprinting techniques, a polymeric structure was replicated. The conclusion is as follows: If the photo-mask was in contact with the GST film and the total energy of laser pulse reached the ablation threshold of the GST film while not over irradiating, then two-dimensional array crystalline marks could be formed on the GST amorphous film. However, the photo-mask does not have any contact with the GST film; the crystalline mark accompanied with the diffraction patterns was formed simultaneously. The etched structure with 40Vf% HNO₃: ethanol etching solution could be fabricated into low surface roughness and precious etched structure then by using 20Vf% HNO₃:DI water etching solution due to ethanol can reduce hydrogen over potential effectively. During the imprinting process, a three dimensional polymeric structure demolded easily from Page 6 of 6

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