Optimization of Ge–Sb–Sn–O Films for Thermal Lithography of Submicron Structures

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Ge–Sb–Sn inorganic resist materials are developed to fabricate submicron structures that have a pattern size smaller than 150 nm and a depth over 100 nm via thermal lithography. The materials are sputtered under Ar:O₂ atmospheres by varying O₂ flow rate and Ge level. Both increasing O₂ flow rate and Ge level can decrease the extinction coefficient, k, at 405 nm wavelength to within a range of 0.58–0.89. Films with appropriate absorption of laser power are chosen to optimize exposure and development processes. A continuous 2.0 mW laser power is used to crystallize the Ge–Sb–Sn–O films. 175-nm-wide and 107-nm-deep grooves are formed after development using alkaline solutions. The 175 nm width is well below half of the 380 nm diffraction limit. A laser pulse strategy is also developed to fabricate discrete dot patterns. By shortening the write 1 time to 0.5 T (7.8 ns), the dot patterns change from oval to round shape. A pit pattern as small as 140 nm diameter and 100 nm depth is achieved.

1. Introduction

Lithography technologies including deep UV lithography,1) near-field lithography,2) interference patterning,3) and electron beam (EB) recording4) have been employed successfully for preparing recording pits on optical discs with higher than 20 GB capacity. These technologies require expensive equipment using shorter wavelength light sources. Organic photoresists are usually chosen for these technologies. However, various problems such as mechanical stability in the case of near-field lithography and slow recording speed for electron beam mastering still exist.5)

Thermal lithography,6,7) also known as phase-transition mastering (PTM),8) transforms an inorganic photoresist layer from the initial state to a transformed state by laser beam heating.5,9) Recording pits can be formed by removing the transformed areas with acid or alkaline solutions. Inorganic photoresists have an advantage of high resolution due to the absorption of laser power are chosen to optimize exposure and development processes. A continuous 2.0 mW laser power is used to crystallize the Ge–Sb–Sn–O films. 175-nm-wide and 107-nm-deep grooves are formed after development using alkaline solutions. The 175 nm width is well below half of the 380 nm diffraction limit. A laser pulse strategy is also developed to fabricate discrete dot patterns. By shortening the write 1 time to 0.5 T (7.8 ns), the dot patterns change from oval to round shape. A pit pattern as small as 140 nm diameter and 100 nm depth is achieved.

To form useful submicron structures via thermal lithography, not only is the phase transformation capability required, but the laser irradiation must also be able to transfer through the thickness of inorganic resist films. Marks with appreciable depth are more difficult to achieve using thermal lithography,11) because the laser heat is scattered while entering the inorganic resist films. Although a small irradiation power could give rise to smaller patterns, the depth of the patterns would be limited. Kokenyesi et al.12) demonstrated that a ∼250 nm bump with 40–50 nm height was obtained using an α-Se/As_S3 nanolayered film. The “bump” is formed due to surface relief during structural transformation. Kojima and Yamada13) showed that using a Sn-doped Ge–Sb–Te phase change material and 450 nm laser irradiation, a mark length of 294 nm with 10 nm thickness is formed using a 50 ns pulse. In many other studies using phase change materials, less than 30-nm-deep patterns were demonstrated. For example, a 110 nm line width with below 35-nm-deep patterns and a 105 nm dot with 25-nm-deep patterns were reported.5) The same research group also demonstrated a volume change thermal lithography technology using TbFeCo–ZnS/SiO₂ multilayer structures. A pattern width of 110 nm was shown, and the pattern thickness can be increased from 55 to 85 nm by annealing.9) In a more recent report14) using a Ge–Sb–Sn–O system, continuous patterns with 170 nm width and 25 nm depth have been reported. Apparently, submicron marks smaller than 150 nm and with a depth higher than 100 nm are rarely reported using thermal lithography.

For a phase change material to obtain such small and deep marks, the speed of phase transition must be increased and the laser absorption of films must be optimized15) for the

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laser heat to penetrate through the bottom of inorganic resist films. Generally, GeTe–Sb$_2$Te$_3$ pseudo binary compounds are widely used as phase change materials for rewritable storage purposes owing to their rapid crystallization speed and thermal stability of amorphous recording marks. To achieve a small pit size, Liu et al. investigated the Sn-doped Ge$_2$Sb$_2$Te$_5$ phase change materials that can be applied for high-speed phase change optical recording media. The addition of Sn to Ge$_2$Sb$_2$Te$_5$ has also been shown to accelerate the speed of crystallization for phase change access memory. Furthermore, a larger optical contrast is demonstrated before and after laser irradiation in the Sn-doped Ge$_2$Sb$_2$Te$_5$, because Sn aids in the stabilization of the crystalline state. In the Ge–Sb–Sn system, Sn is shown to form Sb$_2$Sn$_3$, which could assist the nucleation and accelerate the phase transformation. Therefore, it is of interest to obtain patterns with optimized width and depth combination when Sn-doped GeSb is employed for thermal lithography.

To obtain marks with a large depth and clear edges, the pattern formed by etching crystalline and noncrystalline structures of Ge–Sb–Sn also needs to be clearly differentiated by gaining distinguishable dissolution rates between the two states. This can be achieved by adjusting the optical absorption of the phase change layer for laser irradiation. In this study, we modulate the Ge–Sb–Sn–O inorganic resist film by sputtering with a Ge–Sb–Sn target under Ar/O$_2$ atmosphere. The supply of O$_2$ can affect the absorption of laser power by the films. Furthermore, the O$_2$ level can also increase the dissolution rate difference between the noncrystalline and crystalline states of the films. Procedures for obtaining a minimal structure with >100 nm depth are discussed. The optimized inorganic resist film is intended for making general submicron structures using a traditional 405 nm laser mastering system. If patterns of smaller than 150 nm size and over 100 nm depth can be achieved, the developed Ge–Sb–Sn–O material system could be useful for general submicron structure formation, such as photonic crystal patterning in light-emitting diodes (LEDs) and recording pits in Blu-ray-type discs. Thermal lithography could also greatly reduce the production cost of submicron structures in comparison with other advanced technologies.

2. Experimental Procedure

Pre-grooved polycarbonate (PC) substrates with 740 nm track pitch, 0.6 nm thickness, and 120 nm diameter are used. A 60–80 nm ZnS–20 at. % SiO$_2$ dielectric layer is chosen for substrate protecting and heat buffer purposes in thermal recording. The inorganic resist layer of 80–120 nm Ge–Sb–Sn–O (GSSO) is sequentially deposited using RF magnetron sputtering. The multilayer structures are shown as in Fig. 2(a).

The GSSO films are obtained by RF sputtering a 76.2-mm-diameter Ge–Sb–Sn (GSS) target at a working pressure of $6 \times 10^{-3}$ Torr Ar–O$_2$ atmosphere. Sputtering targets of GSS inorganic resist materials containing 10, 18, and 23 at. % of Ge are employed to understand the effects of Ge upon crystallization of GSSO films. The thicknesses of GSSO films are controlled by adjusting the Ar and O$_2$ gas flow rates and sputtering times. O$_2$ gas flow rates of 25–30 sccm are employed to control the extinction coefficient, which represents the absorption of laser beam energy by GSSO films.

The thickness and optical properties of the multilayer films are measured using an Eta-RT thickness measurement system manufactured by Steag ETA-optik. Laser irradiation is then carried out on the film structures by a PULSTEC ODU-1000 optical disk drive tester using a 405-nm-wavelength laser beam and an objective lens of 0.65 NA. The laser beam exposure is controlled between 1.6 and 8.0 mW power [Fig. 2(b)] at a constant linear velocity of 6.6 m/s. The laser exposure settings are shown in Fig. 3. A line pattern is achieved by continuous laser heating and crystallization of the as-deposited amorphous GSSO while the PC substrate spins.

These crystallized areas are finally dissolved using an alkaline developer to form submicron size grooves [Fig. 2(c)]. The feature size is controlled by regulating laser power and development parameters. The developed patterns are observed using a Digital Instruments Dimension 3100 atomic force microscope (AFM) and a Hitachi S-4700 field-emission scanning electronic microscope (SEM).

Submicron dot patterns are obtained by two-step pulse exposure as shown in Fig. 4. For current laser exposure experiments, each unit pulse (1 T) at 64.5 MHz stands for...
15.5 ns, which corresponds to 102 nm of tracking length. The size of pattern pits can be controlled by parameters including write time and write power.

3. Results and Discussion

3.1 Optical properties of GSSO films

A flat glass substrate is employed to measure GSSO film thickness deviation with disc diameter. It is observed that the thickness deviation of the GSSO film was within 10 nm at the innermost and outmost locations.

For a fixed sputtering time and 100 sccm Ar gas flow rate, O₂ gas was adjusted to control the optical properties of films. Table I lists the sample number, and n and k values of GSSO films at 405 nm by varying Ge levels and O₂ gas flow rate.

The k value apparently decreases with increasing O₂ gas flow rate, while the n value remains relatively unchanged. The dependence of the absorption coefficient (α) on the extinction coefficient k is

$$\alpha = \frac{4\pi k}{\lambda},$$

where λ is the wavelength. The k value is thus proportional to the absorption coefficient of the film at a constant wavelength. Lower k values give rise to films with lower absorption, implying that a higher oxygen content corresponds to a lower absorption for 405 nm laser power. This is, increasing oxygen concentration in films represents a more transparent oxide film. The closer electronegativity between Ge and O can cause the extinction coefficient to drop more than that of the other GSSO films with higher Sn and Sb concentrations, which have a larger electronegativity difference with O.

3.2 Optimized exposure and development process

To investigate the variation of GSSO film during laser exposure, we observe the as-exposed GSSO samples, as shown in Fig. 5. In the exposure process, lasers focus on the land area (Fig. 2) of the PC substrates and cause expansion in the local area of GSSO films. Therefore, Fig. 5(a) demonstrates a convex cross section after laser exposure instead of a flat surface. Top views of these exposed samples are shown in Figs. 5(b) and 5(c). In the SEM observation (Fig. 5(c)), the lighter structures indicate more extruding structures at the center of the land areas (Fig. 2) on the disc substrate. The transformed area apparently deforms in contrast to the outer nonaffected land areas.
The lower oxygen content in GSSO film gives rise to an increased extinction coefficient ($k$) and absorption coefficient ($\alpha$) according to eq. (1). Therefore, the GSS23-A film with higher $k = 0.85$ (Table I) can absorb more energy from the same amount of laser exposure and results in wider thermal diffusion than GSS23-B and GSS23-C with lower $k$ values. The line patterns are thus relatively broadened, as shown in Fig. 6(a) in comparison with Figs. 6(b) and 6(c). In contrast, the samples with the lowest extinction coefficient, e.g., $k = 0.58$ for GSS23-C (Table I), do not absorb sufficient energy from the same 2.2 mW laser irradiation and thus show a smaller and blurry pattern after development [Fig. 6(c)].

Among the GSS23-A–C samples, the developed groove pattern in the GSS23-A sample demonstrates the clearest pattern edge with a smooth groove wall, as shown by the AFM image in Fig. 6(a). The groove contrast also appears to improve with increasing pattern size, which is undesirable. To reduce the pattern size, a lower laser power must be used for exposure.

Further exposures fix the O$_2$ flow rate at 25 sccm and the extinction coefficient ($k$) is kept at 0.85. A series of 1.6, 1.8, 2.0, 2.2, and 2.4 mW laser powers are tested while fixing the development time to control the pattern width. In Fig. 7, the pattern widths obtained are 117, 156, 175, 195, and 234 nm, respectively. It is apparent that increasing laser writing powers increase the volume affected by the heat proportionally. At lower laser powers, patterns are blurred [Fig. 7(a)] owing to incomplete crystallization of GSSO films. To obtain a clear continuous pattern in film structures while keeping the width at minimum, 2.0 mW is needed [Fig. 7(b)]. This bears 175 nm feature width and a depth of 107 nm according to AFM analyses. The 107 nm depth indicates that the developing processes successfully remove the crystallized GSSO film through the entire thickness and form a clear edge at the walls of continuous grooves. This 175-nm-wide groove size is already lower than half of the diffraction limit (0.61 $\lambda$/NA) or 380 nm.

### 3.3 Pulse strategy for dot patterns

To demonstrate the possibility of thermal lithography for making discontinuous patterns using GSSO films, a pulse laser is utilized. According to Fig. 3, the main parameters considered in this study are write 1 time and write power. Figure 8 shows the patterns made by controlling the write 1 time for 0.5 T, 1 T, and 2 T, while keeping the cooling time at 0.5 T, write 2 time at 0.5 T, bottom power at 0.1 mW, and erase power at 0.8 mW. Each unit of 1 T stands for 1/64.5 MHz or 15.5 ns in length under constant linear velocity.

In Fig. 8, dot sizes are shown to increase with writing time, since a longer laser pulse exposure provides more energy over the exposed volume. Further observations demonstrate that the dots elongate along the writing direction. The pit length along the writing direction is larger than the pit width in the radial direction, as shown in Fig. 9. It is reasonable that the longer pulse tends to reserve the heat over a tail along the writing direction. The oval-shaped dot patterns are thus formed [Figs. 8(b) and 8(c)]. Such oval-shaped patterns could cause noise in the signals of recording media. Figure 9 further demonstrates that, with 0.5 T write 1 time and 8.0 mW write power, a nearly round dot pattern can be achieved [Fig. 8(a)]. The minimal size of a less than
300 nm dot pattern is obtained using GSS23-A films with a $k$ value of 0.85. The writing power and size of writing mark are in a similar range to those reported by Song et al.\textsuperscript{30}

To further minimize the size of the dot pattern, we must decrease both the heat affected volume and the write power.\textsuperscript{31} The reduction of the heat affected volume has been shown to vary with reducing the extinction coefficient ($k$) in $3.2$. The $k$ value can be controlled by increasing the O$_2$ flow rate (Table I). Therefore, the GSS23-C film made with a higher O$_2$ flow rate giving a $k$ value of 0.58 is employed. Meanwhile, a reduced power of 4.9–5.9 mW is tested.

Figure 10 shows that, for GSS23-C samples, the dot pattern size decreases proportionally from 250 to 100 nm with the write 1 power decreasing from 5.9 to 4.9 mW. The smaller pattern size confirms that GSS23-C films can be exposed and developed stably at a lower power than GSS23-A films. Although as low as a 100-nm-wide mark is obtained [Fig. 11(b)], the bottom structures of these pits are shown to be less flat [Fig. 11(a)] than that in the 140 nm mark [Fig. 11(c)]. Therefore, an optimum well-defined 140 nm pit size with 100 nm depth is achieved as shown in Figs. 11(d) and 11(e). The pulse laser writing procedures apparently reduce the heat-affected area in thermal lithography and form an even smaller pit size than the continuous mode, as discussed in §3.2. The pattern depth of more than 100 nm is achieved mainly owing to the combination of high crystallization speed and optimized absorption coefficients of the Ge–Sb–Sn–O films.
4. Conclusions

In the current study, experimental results of patterns formed by thermal lithography using inorganic Ge–Sb–Sn–O resist are reported. The absorption of 405-nm-wavelength laser power by Ge–Sb–Sn–O films reduces with increasing O\textsubscript{2} flow rate owing to the formation of amorphous oxide films.

Although a high laser power can improve the pattern contrast after developing, the pattern size also increases with laser writing power. On the other hand, insufficient laser contrast after developing, the pattern size also increases with increasing O\textsubscript{2} flow rate owing to the formation of amorphous oxide films.

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