Thin Solid Films 542 (2013) 409–414

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Physical properties of an oxide photoresist film for submicron pattern lithography☆

Donyau Chiang [a,]*, Chun-Ming Chang [a,d], Shi-Wei Chen [b], Chin-Tien Yang [c], Wen-Jeng Hsueh [d]

[a] Instrument Technology Research Center, National Applied Research Laboratories, Hsinchu, 30076, Taiwan
[b] Nano Science Group, Scientific Research Division, National Synchrotron Radiation Research Center, Hsinchu, 30076, Taiwan
[c] Nanotechnology Research Center, Industrial Technology Research Institute, Hsinchu, 31040, Taiwan
[d] Department of Engineering Science and Ocean Engineering, National Taiwan University, Taipei, 10617, Taiwan

ARTICLE INFO

Article history:
Received 13 August 2012
Received in revised form 31 May 2013
Accepted 31 May 2013
Available online 14 June 2013

Keywords:
Oxide photoresist
Thermal lithography
Direct laser writing
Refraction index
Extinction coefficient
Crystallization activation energy
Sputtering

ABSTRACT

The minimum etched pits of 300 nm diameter and the trenches of 300 nm width with a 50 nm depth for both geometries are prepared in the GeSbSn oxide photoresist on the silicon substrates. The lithographic patterns are recorded by direct laser writing, using a 405 nm laser diode and 0.9 numerical aperture media disc mastering system. The developed pit diameters in an inorganic oxide photoresist are smaller than the exposed laser beam spot diameter due to thermal lithography. The crystal structures of the as-sputtered and the annealed powder samples scraped from the sputtered films are examined by X-ray diffractometer. The effect of the heating rate on the crystallization temperatures is evaluated by a differential scanning calorimeter and the crystallization activation energy is determined from Kissinger's plot. The optical and absorption characteristics of the oxides are strongly dependent on the oxygen flow rate during the reactive magnetron sputtering process. The transmittance of the deposited films increases and the absorption decreases with increasing oxygen flow rate, which implies that at high oxygen flow rate, the film resembles dielectric material. The oxygen flow rate during the deposition process is defined within a limited range to obtain the proper extinction coefficient. The working extinction coefficients of the films ranging from 0.5 to 0.8 are applied in this study to achieve the sharp and vertical edge of the etched pits and trenches of 50 nm depth.

1. Introduction

The sub-micro and nanoscale patterns with different geometric pit or trench dimensions on the photoresist are prepared for a variety of functional optical devices, such as anti-reflectance devices [1,2], photonic crystals [3], biomedical sensors [4], LED patterned sapphire substrate [5,6] and optical memory media [7–9]. The surface patterns in the photoresist can be duplicated by a stamper, which is electroformed from the developed photoresist. This provides a cost effective method to mold inject, to stamp or to imprint the optical devices in a massive production scale. The common lithographic material used to produce the patterns is an organic photoresist containing photoactive radicals. A designed mask shields the unexposed area of the photoresist, and the developed rate of the exposed photoresist heavily depends on the absorption photon dose at a specific exposed light wavelength. The radicals in the organic photoresist can conduct the photo chemical reaction, break the bonds, or agglomerate into polymer structure. Most of the active radicals are susceptible to the exposed light because of the high sensitivity and operation efficient requirements. The developed edges of the marks show an irregular zigzag shape due to the mask shielding effect in the boundary edge. A sharp edge of the developed marks is one of the basic requirements for photoresist applications and careful manipulation is required using the organic photoresist. Another challenge for organic photoresist is the diffraction of the mask. The smaller the holes or openings are in the mask, the more severe the diffractions and the larger the exposed areas are on the photoresist. It is difficult for the developed pits to have sizes smaller than the exposed spot.

Kouchiyama et al. [7,10] proposed an innovative method, known as phase transition mastering (PTM), to produce the nanoscale pattern stamper. With the aid of mold injection technology, plastic objects with sub-micro and nanoscale pattern are manufactured in a cost effective and industrially mature manner. The major innovation of PTM is a phase change material developed for the photoresist application. The thermal lithography phenomenon [11–13] is introduced to explain PTM. The phase transformation temperature, dependent on the exact alloy composition, can be higher than 500 °C. The as-sputtered material film initially deposited on the glass plate is amorphous. The crystallized area usually is in the center and occupies some amount of the laser exposed area and in the crystallized area the temperature is higher than its crystallization temperature. The dissolution rate for the amorphous

---

☆ This is an open-access article distributed under the terms of the Creative Commons Attribution-NonCommercial-No Derivative Works License, which permits non-commercial use, distribution, and reproduction in any medium, provided the original author and source are credited.

* Corresponding author.

0040-6090/$ – see front matter © 2013 The Authors. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.05.134

and crystalline phase in an alkaline solution is significantly different for this phase changed material and the exposed crystalline area, which resembles a positive photoresist, is chemically developed to expose the underneath substrate.

Several inorganic materials were proposed after Kouchiyama performed the thermal lithography. Most of the inorganic photoresist materials published are oxides. Kai and Kouchiyama et al. used transition metal oxides containing molybdenum or tungsten [10]. Ito et al. [8] of Matsushita used TeOx as a positive photoresist. Aoki et al. [9] of Canon used WOx as a negative photoresist and pointed out that oxygen content in the sputtered WOx film is the major factor to obtain molded objects with low noise signal and sharp edge from the developed stamper. Miura et al. [14] of Ricoh used ZnS-SiO_2 as a negative photoresist and HF aqueous solution, instead of alkaline solution, is used to develop the photoresist. Miura's group further applied the dry reactive ion etching method on the obtained ZnS-SiO_2 mask and accomplished a quartz mold [15]. Kurihara et al. [16] of AIST, Japan used PtO_x as an inorganic photoresist material. PtO_x is chemically decomposed into vapor instead of transitioning to solid phase when the irradiated temperature is higher than its decomposition temperature. The decomposition reaction of PtO_x is quick and complete at the decomposition temperature and leaves few residual ashes after the reaction. The only material containing no oxygen was proposed by Shitani et al. [17] of Hitachi. Shitani's group used chalcogenide alloy, which is a common materials applied in the memory layer of optical discs, as a photoresist. Under the proper laser irradiated condition and multilayer structure arrangement, the dot pattern with the size of one-tenth of a laser spot on an approximately 10 nm thick chalcogenide film is demonstrated. However, this approach requires a delicately designed structure of multilayer, which contains a thin layer of photoresist, two dielectric layers and a high thermal conductivity silver layer. The silver layer in the structure is used to modulate the input energy and quickly dissipate the heat to reduce the spot area over the phase transition temperature. Nevertheless, a single photoresist layer, rather than a structure of several layers, is more practical as a lithographic photoresist.

Another innovative oxide photoresist is proposed [18] and is proved to have potential applications to produce sub-micro patterns in certain optical device applications using direct laser writing technology [19,20]. The lithographic mechanisms applied to this oxide photoresist include thermal lithography, phase transformation from the as-sputtered amorphous phase to the crystalline phase irradiated by a recorded laser system and the significant dissolution rate difference between the phases. This oxide material is a multi-species compound containing elements such as Ge, Sn and Sb, but its material properties are not well understood. This study is a comprehensive investigation on the thermal and optical properties of the oxide photoresist material.

2. Experiment

A sputtering target of chemical composition of Ge:Sb:Sn in atomic ratio of 13.5:40:46.5 is used to prepare the deposited films. Unaxis DVD Sprinter is used as the sputtering machine and the deposition conditions are operated under DC reactive magnetron sputtering with oxygen. The background pressure of the chamber is less than 1×10^{-2} Pa. The controlled argon and oxygen flow rates are 35 sccm and 15 sccm respectively, and the sputtering power is 0.3 kW. An inorganic photoresist film of 50 nm thickness is deposited on a silicon wafer and the deposition rate is estimated to be 3.6 nm/s. A commercial disc mastering system with 405 nm laser wavelength and 0.9 numerical aperture conducts the direct laser writing process. The linear recording speed is 3.0 m/sec. The applied laser power levels of 11 mW and 6.5 mW write the individual pit and continuous trench patterns on the photoresist layer, respectively. A NaOH solution of 0.05 M concentration is employed to develop the recorded patterns. The scanning electron microscope (SEM, Hitachi S-4300) with EDX attachment is used to observe the developed surface pattern morphology and to measure the chemical composition of the photoresist. The analyzed compositions and the standard deviation for elements Ge, Sb, Sn and O in this order are 5.48 ± 0.19, 12.75 ± 0.83, 15.03 ± 1.32 and 66.74 ± 2.13 in atomic ratio. All the data are averaged from at least 6 locations in the sample. The operating voltage of SEM is 10 kV.

The thermal properties and the crystallization behavior of this inorganic photoresist are evaluated by the differential scanning calorimeter (DSC, Perkin-Elmer Pyris 1) and x-ray diffractometer (XRD, Material analysis and characterization Co. model M18XHF). Copper target is used to generate X-ray in the XRD measurement. The sample powders for DSC and XRD measurements are scraped from the sputtered film deposited on a glass substrate. The sputtering deposition condition is the same as that described above and a 7.3 μm thick film on a substrate is prepared. The deposition process is interrupted every 40 s and a 3 s cool-down period is added to prevent the film from overheating and to maintain the film material properties. The deposition process continues over 50 cycles to acquire the enough material. A sharp knife blade scrapes the film material on the glass substrate and the scraped powder is collected. The heating rates of 2, 5, 10, 20 and 50 °C/min are performed for the DSC measurements. The sample powders sealed in aluminum pans are heated from ambient temperature to 550 °C under the nitrogen protection atmosphere in DSC. The final crystal structure for XRD measurement is determined from a sample powder annealed at 600 °C for 30 min in a protective atmosphere to ensure the full crystallization. Another GeSbSn alloy, denoted as phase-changed alloy, is prepared without oxygen and is used in comparison with that of the oxide.

The effect of the oxygen flow rate on the optical properties of the deposited films is examined. The argon flow rate is fixed at 35 sccm throughout the deposition process. The oxygen flow rates of 13, 14, 15, 16 and 17 sccm are adjusted to give the partial oxygen pressure to the total pressure ratio of 27.1, 28.6, 30.0, 31.4 and 32.7%. The films with 45 nm thickness and different oxygen contents are deposited on a smooth and flat polycarbonate substrate surface. The reflectance and transmittance of the film assembly are measured by a spectrophotometer (AudioDev ETA-RT model). Wavelengths ranging from 350 nm to 700 nm, which includes the employed laser wavelength of 405 nm for the direct laser writing, are applied to calculate the optical constants of the oxide films.

3. Results and discussions

The laser-written and developed pit pattern on an oxide photoresist is illustrated in Fig. 1, observed by SEM. The individual pit is separated periodically on a silicon wafer. The diameter and depth of each pit are approximately 300 nm and 50 nm, respectively. The pit depth is consistent with the deposited film thickness to ensure the full development of exposed pit. The pit vertical wall shape is sharp and the pit bottom is flat, which confirm the high etching selection between the amorphous and crystalline phases developed by the alkaline solution, observed from the cleavaged cross section view. The theoretical spot diameter of irradiated laser under the laser mastering system is calculated to be 450 nm [21], which is larger than the developed pit diameter. The smaller pit diameter in a thin photoresist layer is realized if a multilayer structure is added [8] and the irradiation power is adjusted appropriately. The inserted diagram at the top left corner of the Fig. 1 illustrates the uniform developed pits arrangement distributed in a large scale area. With this technology, the developed pits can be created easily over an entire regular sized disc. The trench pattern with trapezoid groove is shown in Fig. 2 and the periodical track pitch is approximately 500 nm. The respective upper width and the bottom width of the trapezoid groove are 280 nm and 230 nm. The enlarged diagram to illustrate the detailed geometric dimension of the groove is inserted in the top left corner of figure.