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Ultrafast-laser-induced parallel phase-change nanolithography

Y. Lin, M. H. Hong,[a] and T. C. Chong
Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576, Singapore; Nanoscience and Nanotechnology Initiative, National University of Singapore, 2 Engineering Drive 3, Singapore 117576, Singapore; and Data Storage Institute, 5 Engineering Drive 1, Singapore 117608, Singapore

C. S. Lim
Department of Mechanical Engineering, National University of Singapore, 2, Engineering Drive 3, Singapore 117576, Singapore

G. X. Chen
Nanoscience and Nanotechnology Initiative, National University of Singapore, 2 Engineering Drive 3, Singapore 117576, Singapore

L. S. Tan
Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576, Singapore

Z. B. Wang and L. P. Shi
Data Storage Institute, 5 Engineering Drive 1, Singapore 117608, Singapore

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A phase-change nanolithography technique is developed to fabricate up to millions of two-/three-dimensional nanostructures (~50 nm) over a large area at a high speed by combining femtosecond laser, microlens array, and wet etching process. Near-field scanning optical microscopy, electrical force microscopy, and atomic force microscopy were used to characterize optical and electrical properties of crystalline and amorphous states, respectively. Different reactions of both amorphous and crystalline areas in phase-change film to alkaline solution are demonstrated. Multiphoton absorption and ultrashort pulse contribute to nanostructure generation. This method opens up a route for nanodevice fabrication with phase-change material. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2235855]

A high-throughput and low-cost nanopatterning which allows complete freedom in fabricating nanopatterns is still the target of nanolithography techniques. Electron-beam nanolithography, ion-beam nanolithography, x-ray nanolithography, and near-field scanning probe nanolithography have been developed for decades,[1–4] but they are facing the challenges of low throughput and high cost. Nanoimprint lithography has attracted significant attention for its high throughput.[5] However, it is easy to contaminate expensive stamps, which increases processing cost. In this letter, a parallel phase-change nanolithography technique by an ultrafast femtosecond laser irradiation through a microlens array (MLA) is described. MLA has been demonstrated to pattern micro-/nanostructures uniformly in polymer over a large area within a short time.[6,7] The microlenses (same sizes and focal lengths in micrometer scale) in MLA convert a laser beam into thousands of focal points, which act as array light "pens" for fabricating different tiny structures uniformly over a large area at a high speed. As this is a noncontact parallel nanopatterning process in far field, light diffraction limit is one of the technical obstacles Therefore, femtosecond laser is proposed as the light source to produce fine features, overcoming the optical diffraction limit and fabricate up to millions of nanofeatures through a MLA. On the other hand, a phase-change film was used as the patterned sample in this letter. Phase-change alloys have two phase states of amorphous and crystalline phases (each can be transformed to the other by the heat treatment). The different optical and electrical properties of these two states of phase-change media make it not only widely used in optical data storage, but also as a prime candidate for a random access memory (RAM), which serves as a future alternative to conventional complementary metal-oxide semiconductor (CMOS) based memories.

The phase-change films used are 30 nm thick $Ge_1Sb_2Te_4$ (GST) layers sputtered on polycarbonate substrates. The prepared films are in amorphous phase without annealing. The MLA used is made of fused silica, which consists of 401 $\times$401 lenses in the area of 10×10 mm^2. The diameter of each lens is 23 μm, and the lenses are hexagonally arranged with a pitch of 25 μm. The sag of each lens is 9 μm in height, which is equivalent to the focal length of 28.7 μm. A Ti:sapphire (Spectra Physics Tsunami, mode 3960) femtosecond laser and a regenerative amplifier (Spectra Physics Spitfire, mode 9769A) are used (wavelength $\lambda=800$ nm, pulse duration $\tau=100$ fs, and repetition rate from 1 to 1000 Hz) to irradiate the phase-change films through the MLA. Near-field scanning optical microscopy (NSOM) (Aurora II, Veeco) and atomic force microscopy (AFM) (Digital Instruments D3000) in both AFM mode and electrical force microscopy (EFM) mode are used for characterization. The femtosecond laser power is controlled to avoid ablating film surface but only induce phase change, and the AFM characterization of the features shows no morphology change in the film. The NSOM and EFM are used for characterization of optical and electrical properties, respectively. The light source for the

[a]Author to whom correspondence should be addressed; FAX: (65) 6777 1349; electronic mail: hong_minghui@dsi.a-star.edu.sg

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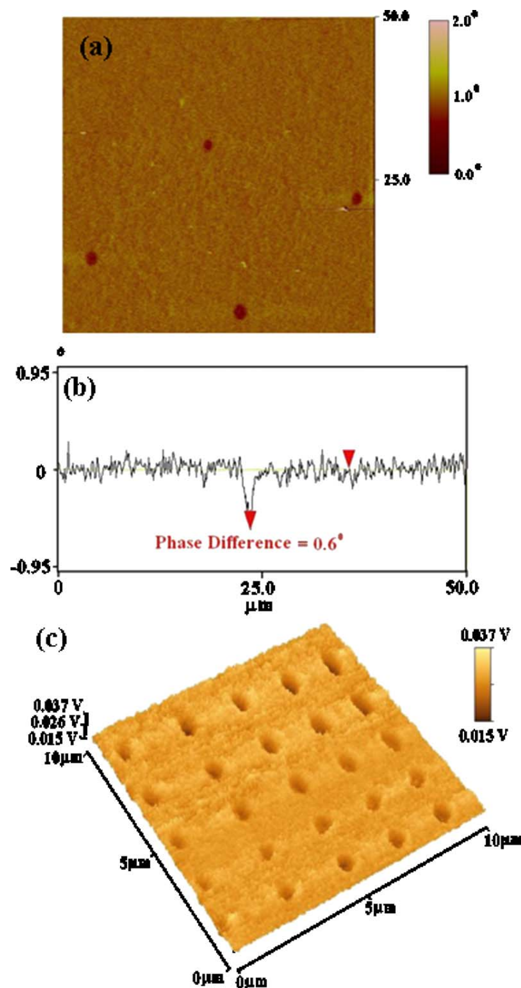

FIG. 1. (Color online) (a) Phase mode EFM image, (b) line profile of one dot feature in (a), and (c) three-dimensional transmission NSOM image of crystalline features in GST film produced by the femtosecond laser irradiation through a MLA at a laser power of 200 mW for 100 ms.

NSOM detection is an argon ion laser (Melles Griot) with a light wavelength of 488 nm.

Figure 1 shows the EFM image in the phase mode, the line profile of one dot feature in EFM image, and the three-dimensional transmission NSOM image of crystalline features in the GST film fabricated by the femtosecond laser irradiation through the MLA with a laser power of 200 mW for 100 ms; the average dot feature size was around 1 μm. The amorphous phase has a much higher resistivity than the crystalline state due to the lower carrier mobility and smaller carrier concentration in the amorphous phase.[8] By applying a voltage of 5 V on the patterned GST film, the conductive probe sensed different electrical forces from crystalline and amorphous phases as shown in Fig. 1(a). The "phase" signal in EFM is the cantilever amplitude signal, which is proportional to the electrical force and resistivity as well. Multiplying the applying voltage and the phase difference, the resistivity difference between amorphous and crystalline can be estimated. The line profile of Fig. 1(b) shows that the phase difference is around 0.6°. Since the voltage is 5 V, the resistivity of amorphous phase in the film is around three times over crystalline phase. This resistivity ratio is high enough to be used in phase-change memory fabrication.[9] On the other hand, the reflectivity and transmitivity of two phase states are also different. Figure 1(c) shows that the crystalline features have lower light transmitivity for its lower photomultiplier tube (PMT) output (in voltage unit). Besides dot array, line array and field emission transistor (FET) structures were also fabricated. Figure 2 is the reflection optical image of FET array structures fabricated at a laser power of 200 mW with the line scanning at a speed of 300 μm/min, and the inset is an enlarged image, where the gate linewidth is around 200 nm.

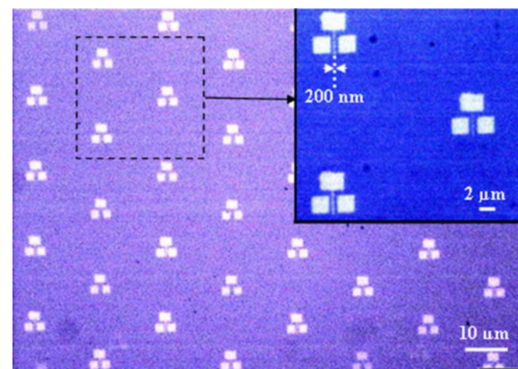

FIG. 2. (Color online) Reflection optical image of the FET structures fabricated in GST film by the femtosecond laser irradiation at a power of 200 mW and a scanning speed of 300 μm/min. The inset is an enlarged image of the features highlighted by dash square.

The amorphous and crystalline states have different reaction speeds to an alkaline solution. This wet etching process develops the two-dimensional nanopatterns in the phase-change film to three-dimensional phase-change nano-

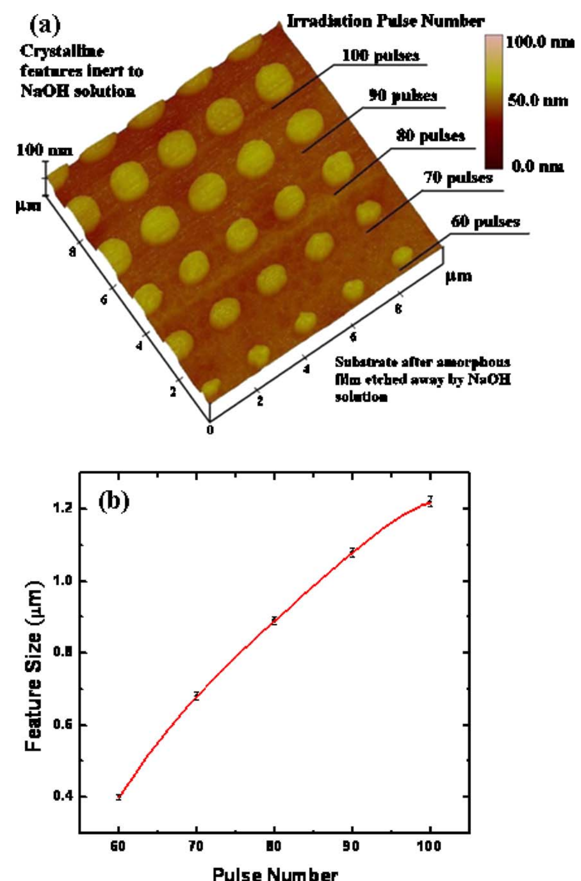

FIG. 3. (Color online) (a) Three-dimensional AFM image of GST film dipped into 30% NaOH solution for 1 min. and (b) the dependence of feature size on exposure time. NaOH solution etched away amorphous areas, and a crystalline pillar array formed. The dot features were fabricated by different irradiation pulse numbers from 60 to 100 at an interval of ten and a laser power of 200 mW.

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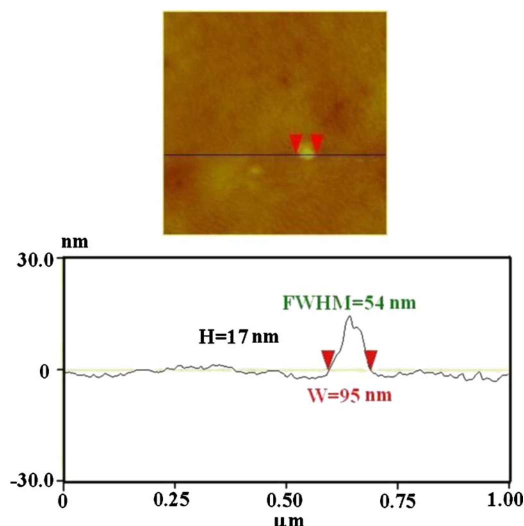

FIG. 4. (Color online) Line profile of one pillar feature with a size of 95 nm, a full width at half maximum (FWHM) of 55 nm, and a height of 17 nm. It was fabricated at a laser power of 80 mW for 50 ms and then dipped into 30% NaOH solution for 1 min.

lithography. Figure 3(a) shows a three-dimensional AFM image of the GST film dipped into 30% NaOH solution for 1 min. The figure also shows the dependence of feature size on exposure time. The dot features were fabricated by different irradiation pulse numbers from 60 to 100 at an interval of ten pulses at a laser power of 200 mW. The feature sizes were 400, 680, 890, 1080, and 1220 nm, respectively. The feature size increased with the number of laser pulses nonlinearly, as shown in Fig. 3(b). The NaOH solution etches away the amorphous area in the GST film, while the crystalline dot features are inert to the chemical solution. The pillar array with the same height of the film thickness (30 nm) is formed, which implies that the amorphous layer has been etched away completely.

According to optical diffraction limit, the minimum beam diameter for 800 nm wavelength laser irradiation after microlens focusing is around 1270 nm. Figure 3 shows that the femtosecond laser irradiation can break the optical diffraction limit and obtain much smaller feature sizes down to 400 nm at a laser power of 200 mW for 60 pulse irradiation. Since phase-change transformation is determined by temperature, lower laser power and fewer pulses transfer less laser energy to the sample. Figure 4 shows the line profile of a dot feature of 95 nm with its full width at half maximum (FWHM) of 55 nm and height of 17 nm. The irradiation laser power was 80 mW and pulse number was 50. The film was dipped into 30% NaOH solution for 1 min. Different from the pillar shape features observed in Fig. 3, this sub-100 nm feature was more like a hill shape, and the height was much smaller than 30 nm (film thickness). This is partly due to much lower laser power and fewer irradiation pulses, while the effects of femtosecond laser and heat flow dynamics in the phase-change film play key roles. Phase-change recording is a thermal-mode recording processes. The heat transferred by the laser irradiation redistributes in the film through thermal diffusion before the laser pulse ends. However, the pulse duration of femtosecond laser is much shorter than the thermal diffusion time, which can result in incomplete redistribution of absorbed laser energy in both horizontal and vertical directions. Femtosecond laser has proven its ability to produce fine features in photolithography for ultrashort pulse and extremely high peak power intensity.[10–15] The ultrashort pulse duration of femtosecond laser induces multiphoton absorption (MPA) effect, which makes the absorption coefficient much less than single-photon absorption. Such nonlinear effect is capable of confining the high optical intensity in a miniaturized region. Meanwhile, ultrashort pulse duration makes the energy for the sample heating deposit in less than 100 fs (10^{-13} s) with a rapid cooling rate.[16] Steep temperature gradient makes it difficult for heat flowing and thus confines the heat inside a smaller area of the phase-change film. Incomplete phase-change transformation is aggravated by the low laser power and fewer irradiation pulses. It leads to the “hill” shape rather than the pillar shape of crystalline feature with 55 nm FWHM. Such phase-change nanolithography demonstrates its advantages over other lithography techniques with its high speed and uniform nanopatterning over a large area for the high-throughput and low-cost nanodevice fabrication.

In conclusion, parallel phase-change nanolithography by a femtosecond laser irradiation through a microlens array was developed. By making use of alkaline solution, three-dimensional nanostructures were fabricated in $Ge_1Sb_2Te_4$ phase-change films. Due to the ultrashort pulse duration and multiphoton absorption of femtosecond laser as well as thermal mode recording mechanism of phase-change films, features with the FWHM of 55 nm were obtained. The feature size can be compared with those fabricated by near-field techniques. The high throughput and low cost of this phase-change nanolithography make it a highly potential method for future nanodevice fabrication.

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