Applied Surface Science 316 (2014) 9–14

Contents lists available at ScienceDirect

Applied Surface Science

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

Femtosecond laser-induced nanoperiodic structures and simultaneous crystallization in amorphous indium-tin-oxide thin films

C.W. Cheng[a,*], I.M. Lee[b], J.S. Chen[b,c]

[a] Department of Mechanical Engineering, National Chiao Tung University, No. 1001, Ta Hsueh Road, Hsinchu 30010, Taiwan, ROC
[b] Department of Mechanical Engineering, National Chung Cheng University, No. 168, University Rd., Min-Hsiung, Chia-Yi 621, Taiwan, ROC
[c] Department of Mechanical Engineering, National Chung Hsing University, 250 Kuo Kuang Rd., Taichung 402, Taiwan, ROC

ARTICLE INFO

Article history:
Received 28 April 2014
Received in revised form 29 June 2014
Accepted 12 July 2014
Available online 12 August 2014

Keywords:
Femtosecond laser
Nanoperiodic structure
Crystallization
Indium-tin-oxide

ABSTRACT

Fabrication of crystalline indium-tin-oxide (c-ITO) nanogratings and smooth line patterns on amorphous ITO (a-ITO) thin films by femtosecond laser-induced structuring and simultaneous crystallization followed by chemical etching is demonstrated. Three types of c-ITO structures are obtained merely by controlling the laser pulse energy of a high-repetition rate femtosecond laser at wavelength 532 nm: nanogratings perpendicular to laser polarization direction with period of 130 ± 11 nm, smooth c-ITO line patterns as well as nanogratings parallel to laser polarization direction with period of 390 ± 10 nm. Large area c-ITO patterns and nanograting structures are fabricated, which are expected to be used in optoelectronic and micro-electronic devices.

1. Introduction

Femtosecond laser material processing has been demonstrated as a novel approach for surface micro- and nano-machining of bulk materials [1] and internal modification of transparent materials [2] due to a minimal heat-affected zone and nonlinear multi-photon absorption. Besides bulk materials, femtosecond laser annealing (FLA) for thin films is investigated in order to improve optical or electrical efficiency. Researchers have used femtosecond laser pulses to anneal amorphous silicon (a-Si) films [3,4] or hydrogenated (a-Si:H) films [5], based on femtosecond laser-induced crystallization or the FLA process. Very recently, polycrystalline silicon thin film transistors, fabricated on channels crystallized by near-infrared FLA, were demonstrated [6]. Femtosecond laser pulses are further demonstrated to be able to produce non-regular microstructures [7] or nanostructures [8,9] and simultaneous crystallization of a-Si thin film in one-step processing. Non-periodic crystalline structures, having light trapping capabilities, were presented.

Recently, the use of pico- or femtosecond pulses for processing of thin films of transparent conducting oxide such as ITO has been investigated with convincing results. The laser ablation process for use in patterning ITO thin film was presented [10–15], i.e. selectively removing the ITO and leaving the desired ITO pattern as transparent electrodes for devices. Since amorphous ITO (a-ITO) thin films have a more rapid etching rate than crystalline ITO (c-ITO) structures do [16], a high-repetition rate (≥80 MHz) FLA process, followed by chemical etching, was used to anneal and structure a-ITO [17] or polycrystalline ITO film [18,19]. In our previous work [20], it was found that sub-micro c-ITO grating from a-ITO thin film based on the laser-induced periodic surface structure (LIPSS) combined with crystallization, was achieved. The periodic-like c-ITO nanostructures were found to have a period of approximately 200 nm (i.e. one-quarter of the irradiation wavelength 800 nm) and were perpendicular to the laser polarization direction. Recently, Leu et al. [21] used a low repetition rate (5 kHz) femtosecond laser to fabricate self-organized nanodots and a periodic ripple pattern (perpendicular to the laser polarization direction) on ITO film; the local conductivity was significantly higher than that of the as-deposited ITO film. Afshar et al. [18] used a high-repetition rate femtosecond laser to structure polycrystalline ITO film; the periodic structures were also perpendicular to the laser polarization direction.

In this study, c-ITO nanogratings either parallel or perpendicular to the laser polarization direction are obtained from a-ITO thin film by high-repetition rate femtosecond laser (wavelength 532 nm) irradiation, followed by chemical etching. The results show that by careful control of the laser fluence, three types of c-ITO

* Corresponding author. Tel.: +886 3 5712121 55126; fax: +886 3 5720634.
E-mail address: weicheng@nctu.edu.tw (C.W. Cheng).

http://dx.doi.org/10.1016/j.apsusc.2014.07.071
0169-4332/

structures can be obtained: nanogratings perpendicular to polarization direction, a smooth c-ITO line pattern and nanogratings parallel to polarization direction. Furthermore, a large area c-ITO pattern and nanograting structures are demonstrated.

2. Experimental procedure

Amorphous ITO thin films with a thickness of approximately 100 nm were deposited on glass substrates (NEG OA10) using a DC magnetron sputtering system using the In_2O_3 (90 wt%):SnO_2 (10 wt%) target. The thin films were then irradiated using a variable repetition rate femtosecond fiber laser (FemtoPower 1060-3uJ-s, Fianium Inc.) with a double-frequency wavelength of 532 nm, a pulse width <500 fs, a variable repetition rate 0.01–1 MHz and a maximum pulse energy of ~3 μJ used for annealing the a-ITO thin film in air. The laser beam entered an objective lens (numerical aperture 0.26, M Plan Apo NIR, Mitutoyo), and was subsequently incident in the normal direction on the surface of an a-ITO-coated specimen mounted on an *X*–*Y* positioning stage. The focal spot diameter on the specimen surface was approximately 3.5 μm. The structures were then fabricated by translating the sample stage under the control of a PC-based micro-positioning system with precision better than 1 μm.

After laser processing, the samples were immersed in a 0.05 mol/L oxalic acid etchant at 50 °C for 2 min. Due to the more rapid etching rate of the a-ITO thin film than the c-ITO structure [16], the etching process resulted in the complete removal of the non-irradiated a-ITO film, leaving only the crystalline c-ITO pattern. The laser-irradiated area (before and after etching) of the surface was observed by optical microscopy and scanning electron microscopy (SEM). The structural and optical properties were measured by X-ray diffraction method (XRD, Bruker Smart APEX CCD X-ray) and spectrophotometer, respectively.

3. Results and discussion

Fig. 1shows the top-view SEM images of the ITO structures (a section of a line pattern) formed at a laser pulse energy of 536 nJ (laser fluence 5.57 J/cm^2) with a laser repetition rate of 0.5 MHz, and scanning speed of 0.25 mm/s, 2.5 mm/s and 25 mm/s with linearly polarized light (*E*) orientated in the perpendicular direction to the scanning path, respectively. Note, that Fig. 1(a)–(c) and (d)–(f) was obtained before and after chemical etching, respectively. The equivalent number (*N*) of pulses applied to an assumed single laser spot on the ITO film is estimated by $N = D_e f/v_s$, where D_e is the diameter of the laser spot on the target surface, *f* is the laser repetition rate and v_s is the scanning speed. For example, when $D_e = 3.5$ μm and $f = 0.5$ MHz, the *N* is 7000, 700 and 70 for the scanning speed v_s of 0.25 mm/s, 2.5 mm/s and 25 mm/s, respectively.

In Fig. 1(a) and (b), few nanostructures were found at the center of the line pattern. Fig. 2 shows the high magnification SEM image of the center area of Fig. 1(a)–(c), respectively. As seen in Fig. 2(a) and (b), the periodic-like ITO nanostructures perpendicular to the laser polarization, under an average period of 130 ± 11 nm were formed, which is about four times smaller than the laser wavelength (532 nm). The formation of the LIPSS may be attributed to the optical interference of incident femtosecond laser irradiation (single beam) and the surface plasmon wave. The period of the nanostructures is near $\lambda/2n$, where λ is the wavelength of the incident laser, and *n* is the refractive index of the irradiated material. In this study, λ was 532 nm and *n* was ~2, under calculated periods of 133 nm, which is close to the experimental data (130 ± 11 nm). A more detailed discussion can be found in an earlier study [20]. In Fig. 2(c), since the laser fluences were below the ablation threshold, no nanostructures were found in the irradiated area.

As seen in Fig. 1(d)–(f), the unirradiated a-ITO area was removed by an etching solution to form a c-ITO structure on the glass substrate. In Fig. 1(d) and (e), the nanostructures at the center area of the line pattern were retained on the glass substrate after etching, and the nanostructures were crystalline. This means that when the a-ITO thin film was irradiated with a single femtosecond laser beam at an appropriate laser fluence (usually near the ablation threshold), a periodic-like c-ITO structure was formed based on the LIPSS combined with femtosecond laser-induced crystallization in a single process. Moreover, since the irradiation intensity of the laser beam has a Gaussian distribution, the outer edges of the irradiated paths are subjected to a lower energy input; thus, it can be seen that the center areas of the periodic-like a-ITO structures

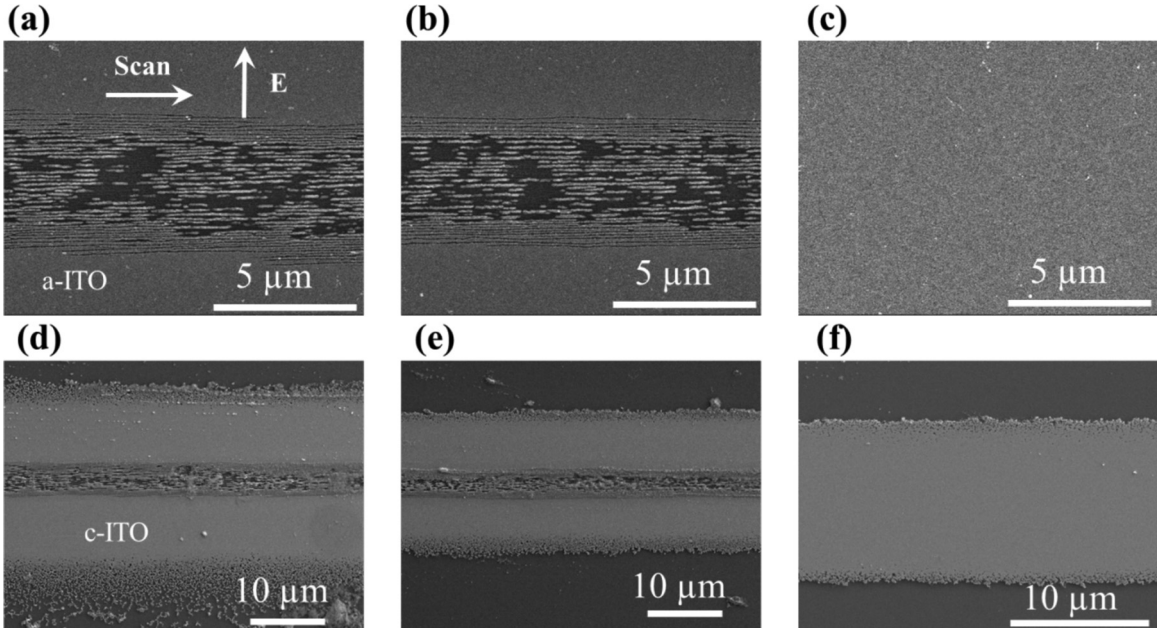

Fig. 1. SEM images of ITO structures formed at laser pulse energy 536 nJ, laser repetition rate 0.5 MHz and scanning speed of (a, d) 0.25 mm/s, (b, e) 2.5 mm/s, (c, f) 25 mm/s. Note, that (a)–(c) and (d)–(f) are obtained before and after chemical etching, respectively.