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Patterning crystalline indium tin oxide by high repetition rate femtosecond laser-induced crystallization

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ABSTRACT

A method is proposed for patterning crystalline indium tin oxide (c-ITO) patterns on amorphous ITO (a-ITO) thin films by femtosecond laser irradiation at 80 MHz repetition rate followed by chemical etching. In the proposed approach, the a-ITO film is transformed into a c-ITO film over a predetermined area via the heat accumulation energy supplied by the high repetition rate laser beam, and the unirradiated a-ITO film is then removed using an acidic etchant solution. The fabricated c-ITO patterns are observed using scanning electron microscopy and cross-sectional transmission electron microscopy. The crystalline, optical, electrical properties were measured by X-ray diffraction, spectrophotometer, and four point probe station, respectively. The experimental results show that a high repetition rate reduces thermal shock and yields a corresponding improvement in the surface properties of the c-ITO patterns.

1. Introduction

In order to improve the device characteristics of optoelectronic products such as flat-panel displays, solar cells and touch panels, the amorphous transparent conducting oxide (TCO) materials used in the fabrication of such products are transformed into a crystalline material via a thermal annealing process in order to reduce their resistivity and enhance their transparency. Indium tin oxide (ITO) is one of the most widely-used TCO materials, and thus the development of rapid and precise c-ITO patterning techniques has attracted significant interest in recent decades.

Conventionally, c-ITO patterns are fabricated via the photolithography of a-ITO thin film followed by a thermal annealing process (>200 °C) [1]. However, this approach has the disadvantage of multiple and high-cost processes. Thus, the feasibility of using a direct laser ablation technique to pattern the ITO film by removing the undesired portion of the thin film has significant appeal. As a result, the literature contains many investigations into the application of both long-pulse (i.e. nanosecond) [2–8] and ultra-short pulse (i.e. picosecond or femtosecond) [9–12] laser systems for patterning purposes. However, the ablation process requires a finite amount of laser fluence to evaporate the workpiece material, and thus usually results in the formation of elevated ridges at the edge of the ablation path and defects in the layers below. In [13], the authors utilized a low repetition rate nanosecond excimer laser (wavelength 308 nm, LPX 240, Lambda Physics) to pattern ITO films via a laser annealing. However, the results showed that they did not succeed in crystallizing a-ITO layers on glass substrate without cracking, because of thermal shocks.

This study proposes a two-step technique for fabricating ridge-free and crack-less c-ITO patterns using a high repetition rate femtosecond laser-induced crystallization process. In the proposed approach, the desired area of the ITO film is transformed from an amorphous structure to a crystalline structure via femtosecond laser irradiation. The patterned ITO film is then etched in an oxalic acid solution to remove the unwanted a-ITO regions since the etching rates of a-ITO and c-ITO in chemicals are much different [14].

2. Experiments

The experiments were performed using an Ti:Sapphire laser (Mai-Tai, Spectra-Physics) with a central wavelength of 800 nm, a repetition rate of 80 MHz, and a pulse duration of ~100 fs. The energy of the linear polarized Gaussian laser beam was attenuated initially by a rotatable half-wave plate and a polarizing beam splitter. The laser energy was measured by passing the polarized light beam through a beam splitter and routing the reflected component to a power detector. Meanwhile, the transmitted laser beam was passed through a mechanical shutter and reflective mirror system such that it entered an objective lens (numerical aperture 0.26, M Plan Apo NIR, Mitutoyo) and was incident in the normal direction on the surface of the a-ITO coated specimen mounted on an *X–Y* axis

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stage. The focal spot size on the specimen surface was adjusted to a diameter of approximately ~5 µm. In the present experiments, a-ITO thin films with a thickness of ~100 nm were deposited on glass substrates (NEG OA10) by a DC magnetron sputtering system using the In_2O_3 (90 wt%):SnO_2(10 wt%) target.

The c-ITO structures were fabricated by translating the sample stage under the control of a PC-based micro-positioning system with an accuracy of better than 1 µm. After the laser-induced crystallization process, the samples were immersed in a 0.1 N oxalic acid etchant at 50 °C for 2.5 min. After etching, the processed area of the surface was observed by scanning electron microscopy (SEM, FE-SEM 7001) operated at 15 kV, and the cross-sectional observation of the crystalline area was performed by transmission electron microscopy (TEM, FEI Tecnai G^2 20 S-Twin) operated at 200 kV. Cross-sectional TEM samples perpendicular to the c-ITO line pattern were prepared by focused ion beam (FIB, SMI 3050) micromachining, the FIB with a gallium ion source was used to mill the c-ITO down to a thickness 100–200 nm in order to make cross-section sample. The crystalline, optical properties and electrical resistivity were measured by X-ray diffraction method (XRD, Bruker Smart APEX CCD X-ray), the X-ray radiation source used is Cu-Kα radiation, the scan speed is 4°/min and scan range is 20°–60° at room temperature, spectrophotometer and four point probe station, respectively.

3. Results and discussion

Fig. 1 shows the SEM images of the c-ITO line patterns fabricated with a constant scanning speed of 50 mm/s and laser powers in the range 180–240 mW. Note that the specimen is in an etched condition. It can be seen that the a-ITO area is removed after chemical etching and the c-ITO line pattern is retained on the glass substrate. It was found that the width of c-ITO line increased with increasing irradiated laser power, and the c-ITO lines have ridge free at edge and crack-less characteristics. High magnification SEM images of the as deposited a-ITO thin film and

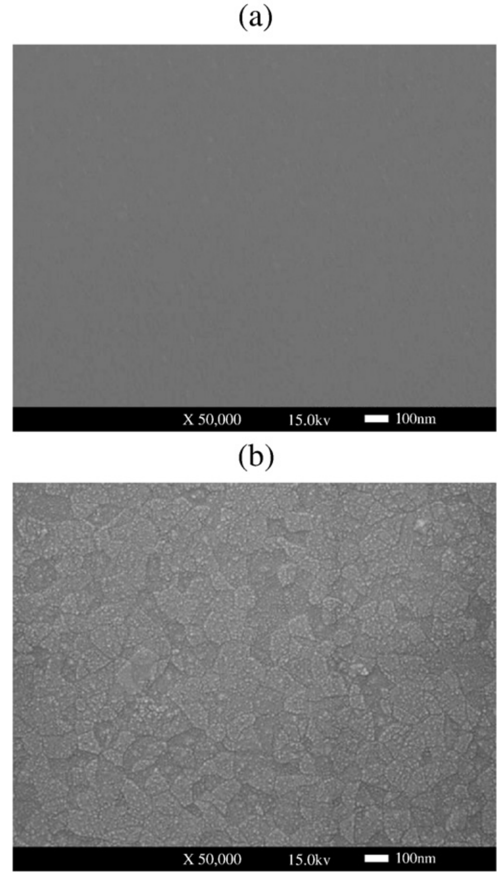

Fig. 2. SEM images: (a) as-deposited a-ITO thin film surface, (b) c-ITO line pattern of Fig. 1 (magnification 50,000×).

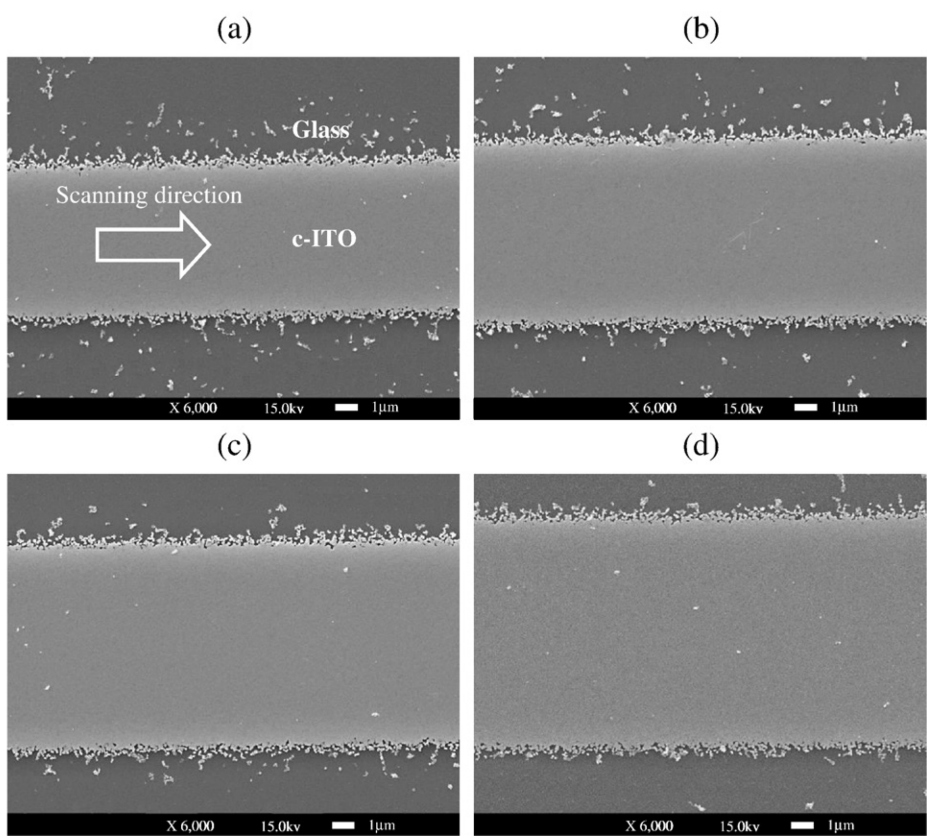

Fig. 1. SEM images of c-ITO line patterns fabricated with laser powers of (a) 180 mW, (b) 200 mW, (c) 220 mW, (d) 240 mW (magnification 6000×).