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Performance optimization of fluorine-doped tin oxide thin films by introducing ultrasonic vibration during laser annealing

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ABSTRACT

Commercial fluorine-doped tin oxide (FTO) thin films were subjected to laser annealing coupled with ultrasonic vibration (48 kHz and 350 W). The effects of ultrasonic vibration, laser fluence and defocusing amount were systematically studied. Laser annealing could result in grain growth or damage of the FTO layer, and introducing ultrasonic vibration during laser annealing could effectively enhance the film compactness, decrease the film thickness and refine the grains in the film. As a result, the optical and electrical properties of the ultrasonic-vibration-assisted laser-annealed FTO films were significantly improved by using low laser fluences and high defocusing amounts, and were slightly deteriorated when high laser fluences and low defocusing amounts were adopted. The results indicated that the film obtained by ultrasonic-vibration-assisted laser annealing using a laser fluence of 0.6 J/cm^2 and a defocusing amount of 2.0 mm had the best overall photoelectric property with an average transmittance of 84.1%, a sheet resistance of 8.9 Ω/sq and a figure of merit of 1.99×10^{-2} Ω^{-1}, outperforming that of the film obtained by pure laser annealing using the same experimental parameters. The present study confirms the efficacy of ultrasonic-vibration-assisted laser annealing in optimizing performance of FTO films.

1. Introduction

Transparent conducting oxide (TCO) materials on glass or flexible plastic substrates have attracted more and more academic and industrial interests owing to their multiple properties such as excellent optical transparency and good electrical conductivity [1]. Until now, most TCO materials are based on tin oxide (SnO_2), indium tin oxide (In_2O_3), zinc oxide (ZnO) or their mixed compounds. Among these TCOs, fluorine-doped tin oxide (FTO) has the virtues of abundance, non-toxicity, low cost, good thermal stability and high chemical inertness [2,3], enabling it to be widely used in various optoelectronic device applications including solar cells [4], flat-panel displays [5], light-emitting diodes [6] and gas sensors [7].

The rapid development of optoelectronic devices has prompted researches on developing more excellent FTO thin films since the FTO films prepared by traditional deposition methods can hardly satisfy the practical application requirements [8]. Further performance optimization of FTO films has been confirmed to be experimentally feasible [9], and most of the optimization strategies have involved furnace thermal annealing [10–12] and laser annealing [13–15]. Both furnace thermal annealing and laser annealing can lead to elimination of defects and even recrystallization, thereby improving photoelectric properties of FTO films [10,13]. However, it is commonly accepted that laser annealing outperforms furnace thermal annealing in flexible selectivity, shortening operation time and avoiding damages to substrates [16,17]. Furthermore, the gradient temperature distribution in film samples during laser annealing will prevent the escape of doping elements in the films and restrain the diffusion of impurities from the substrates [18], therefore avoid degeneration of the film conductivity. Due to these advantages, laser annealing of FTO films has been extensively studied. On the other hand, it is notable that achieving preparation of well compacted and highly uniform thin films by various deposition methods coupled with ultrasonic vibration has been addressed [19–24], but laser annealing under ultrasonic vibration for optimizing film performance has not been reported. As suggested by previous researches [19,20], ultrasonic vibration applied in deposition process has

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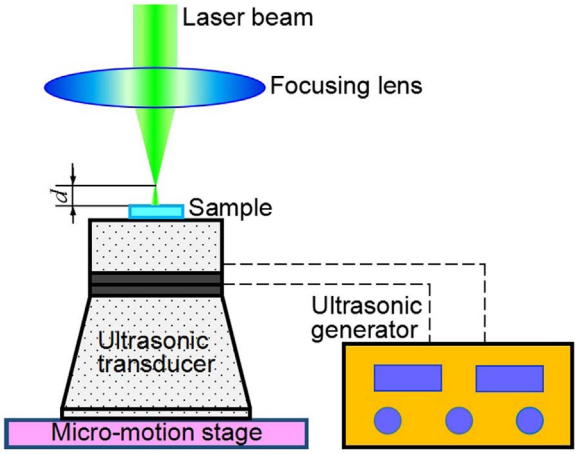

Fig. 1. Schematic diagram of the ultrasonic-vibration-assisted laser annealing setup.

a positive effect on enhancing film compactness and improving crystal quality, so it is also expected that the ultrasonic vibration introduced during laser annealing will help form a more compact film layer with optimized crystallinity, thus yielding higher optical transmittance and electrical conductivity of the films.

In the present work, we propose an ultrasonic-vibration-assisted laser annealing process to achieve performance optimization of FTO thin films. More specifically, commercial FTO thin films with glass substrates were placed on the top surface of an ultrasonic transducer and subsequently annealed by a 532 nm nanosecond pulsed laser. The influences of laser fluence and defocusing amount on surface morphology, film thickness, crystal structure, transmittance and sheet resistance of the films were investigated. A pure (ultrasonic-vibration-free) laser-annealed FTO film was also prepared for comparison.

2. Experiment

The commercial FTO glass pieces (15 mm×15 mm) were cleaned ultrasonically with deionized water, acetone and anhydrous ethanol each for 10 min, and then dried in a high-purity (99.99%) nitrogen gas stream. The as-cleaned FTO glass pieces were used as the film samples to undergo ultrasonic-vibration-assisted laser annealing. Fig. 1 shows the schematic diagram of the ultrasonic-vibration-assisted laser annealing setup. Firstly, the FTO film samples were fixed on the top surface of an ultrasonic transducer with double-sided tape. The ultrasonic transducer with a constant frequency of 48 kHz was placed on a micro-motion stage and connected to an ultrasonic generator with an input vibration power of 350 W. Subsequently, a laser beam output by a diode pumped Nd:YVO_4 nanosecond pulsed laser was vertically irradiated on the film sample surface after being focused by a focusing lens with a focal length of 100 mm. The central wavelength and the repetition rate of the laser beam were 532 nm and 1 kHz, respectively. The sample surface was located below the focal spot of laser beam with a certain defocusing amount (d), which can be adjusted by precisely controlling the position of the micro-motion stage through a computer program. Finally, the laser beam scanned back and forth along the x-axis with a spot size of 100 μm, a scan line spacing of 20 μm and a scanning speed of 20 mm/s. The laser power can be adjusted by a PC-based controller to any desired intensity for laser annealing of the FTO films.

The unannealed FTO film sample was numbered as F. Two groups of FTO film samples were prepared by ultrasonic-vibration-assisted laser annealing. In one group, the value of defocusing amount, d, was kept at 2.0 mm and various laser fluence (F) values (i.e. 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 J/cm^2) were adopted. These samples were respectively numbered as ULF1, ULF2, ULF3, ULF4, ULF5 and ULF6. In another group, the F value was fixed at 0.6 J/cm^2 and various d values (i.e. 0.5, 1.0, 1.5, 2.5, 3.0 and 3.5 mm) were employed. These samples were respectively denoted as ULF7, ULF8, ULF9, ULF10, ULF11 and ULF12. In addition, for comparison, an FTO film sample was laser annealed using F=0.6 J/cm^2 and d=0.2 mm without ultrasonic vibration and expressed as LF.

The top-view and cross-sectional images of the film samples were observed by a scanning electron microscope (SEM, Hitachi S-3400N). The average particle sizes (D_p) on the sample surfaces were estimated from SEM images by the Nano Measure 1.2 free software. An X-ray diffractometer (XRD, Bruker D8 Advance) with Cu-Kα radiation (λ=0.1541 nm) was used to ascertain the crystal phases of the film samples. The optical transmittance spectra of the samples were obtained through a UV–Vis spectrophotometer (Shanghai Yuanxi UV-8000). The sheet resistances of the samples were measured using a digital four-point probe instrument (Guangzhou Four Probes Tech RTS-9).

3. Results and discussion

3.1. Surface morphology and film thickness

The photoelectric properties of the FTO films significantly depend on their surface morphology. Fig. 2 presents the top-view SEM images of the unannealed FTO film (sample F) and the pure laser-annealed FTO film (sample LF). It was seen that the unannealed FTO film exhibited a rough surface that contained pyramid-shaped particles with sharp edges and an average particle size of ~310 nm (Fig. 2a). The particles were non-uniformly and sparsely distributed to generate some

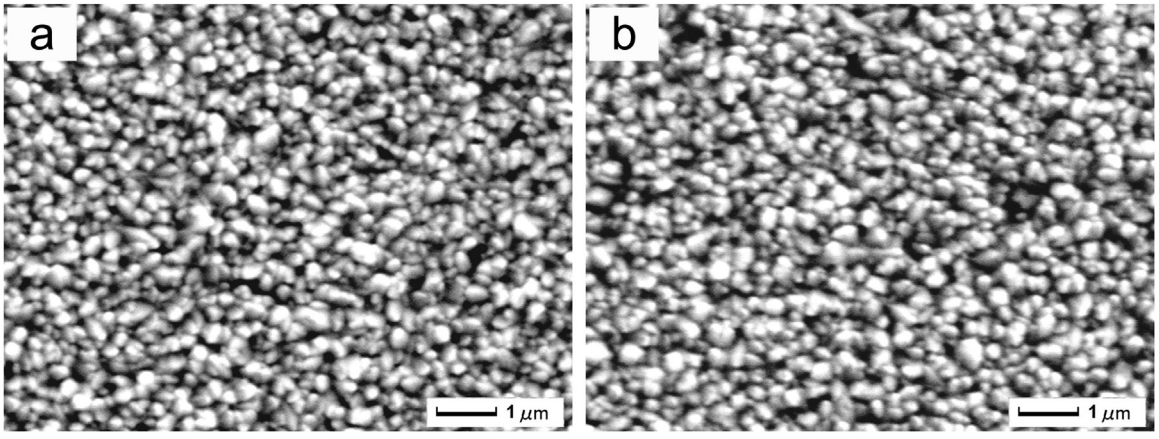

Fig. 2. Top-view SEM images of (a) the unannealed FTO film (sample F) and (b) the pure laser-annealed FTO film using a defocusing amount of 2.0 mm and a laser fluence of 0.6 J/cm^2 (sample LF).