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# Ultraviolet laser ablation of fluorine-doped tin oxide thin films for dye-sensitized back-contact solar cells

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ABSTRACT

In this study, laser ablation of a fluorine-doped tin oxide (FTO) thin film on a glass substrate was conducted using a 355 nm Nd:$YVO_4$ ultraviolet (UV) laser to obtain a 4×4 mm microstructure. The microstructure contains a symmetric set of interdigitated FTO finger electrodes of a monolithic back-contact dye-sensitized solar cell (BC-DSC) on a common substrate. The effects of UV laser ablation parameters (such as laser fluence, repetition frequency, and scanning speed) on the size precision and quality of the microstructure were investigated using a 4×4 orthogonal design and an assistant experimental design. The incident photon-to-electron conversion efficiency and the current–voltage characteristics of the BC-DSC base of the interdigitated FTO finger electrodes were also determined. The experimental results show that an FTO film microstructure with high precision and good quality can be produced on a glass substrate via laser ablation with high scanning speed, high repetition frequency, and appropriate laser fluence.

## 1. Introduction

Dye-sensitized solar cells (DSCs) have recently attracted considerable attention due to their simple fabrication processes and low fabrication costs [1–3]. Transparent conductive substrates play an important role in achieving the high optical transmittance and low resistivity required in a functional DSC [4]. Two kinds of transparent conductive oxides (TCOs) are widely used in the DSC: indium-doped tin oxides (ITOs) and fluorine-doped tin oxides (FTOs). FTO is superior to ITO because the former has low and temperature-stable resistivity [5,6].

In 2010, Fu et al. [7] reported the fabrication process of a monolithic, back-contact, dye-sensitized solar cell (BC-DSC) with an array of two interdigitated finger electrodes. Both the working and counter electrodes were placed onto the same substrate to efficiently extract photogenerated positive and negative charges from an overlying dye-sensitized heterojunction (Fig. 1). In such structures, the effective area of the electrodes was slightly sacrificed. However, the BC-DSC can prevent optical transmission losses because of the reduction in the conductive glass substrate. In addition, several cheap and opaque substrate materials with good conductivity can be used. Furthermore, the large-scale fabrication of interdigitated finger electrodes can be easily realized, which significantly reduces the cost of the BC-DSC and promotes the commercialization of the DSC to a large extent. Such back-contact concepts have been applied in improving the performance of silicon cells [8]. The quality of these microstructured electrodes determines the performance of the BC-DSC fabricated via conventional photolithography techniques [7]. However, these techniques have several disadvantages that are likely to limit their applications in commercial DSC production. The disadvantages include (1) the sequential use of several masks to fabricate a set of 4×4 mm microstructured electrodes decreases the efficiency of the system and results in quality defects; (2) it is difficult to apply these techniques in the fabrication of a large BC-DSC; and (3) the manufacturing cost is very high.

Numerous studies on laser ablation have been conducted. Different laser systems were used to process the TCO thin film layers on glass substrates. Chen et al. [9] described the pulsed ultraviolet (UV) laser ablation characteristics of ITO thin films on glass substrates. They reported that the laser repetition frequency and scanning speed affected the spot overlap rate and the ablation width. Chen et al. [10] conducted similar investigations on both glass and polycarbonate substrates. Farson et al. [11] proposed the ablation of ITO films using a 755 nm Ti:sapphire laser with a repetition rate of 2 kHz and a pulse width of 150 fs. Kim et al. [12] studied the ablation of FTO thin-film layers using a simple pulsed 1064 nm laser with a Gaussian mode generated using a pin-hole inserted within the laser resonator. These studies had expounded the characteristics and principles of laser ablation on TCO thin films at different degrees. However, the following issues exist in these studies: (1) most of the previous laser ablation studies only focused on ITO thin films in the manufacturing of flat panel displays; (2) the pulse repetition frequencies of the aforementioned laser systems were less than 10 kHz, making the laser scanning speed too low to achieve high microprocessing efficiency; and (3) these studies only focused on the investigations of

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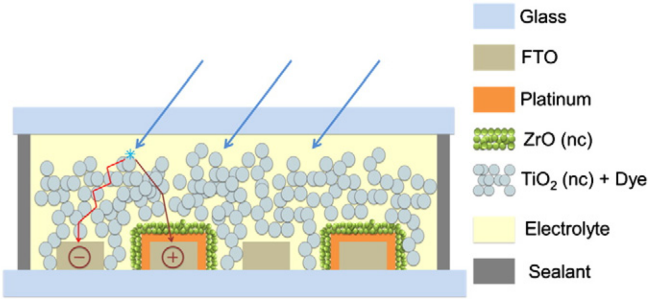

**Fig. 1.** Schematic device configurations of a simple back-contact dye-sensitized solar cell.

a simple ablation line, in which differences in the microfabrication of FTO thin films exist.

It has been reported that the UV light absorption rate of FTO glass is bigger than that of the near-infrared region [13], and the focal spot size of UV laser is smaller than that of near-infrared laser when the parameters of optical systems are fixed. In the present work, a third-harmonic Nd:YVO$_4$ laser microprocessing system – which has high resolution, high precision, high flexibility without using any mask, high efficiency, and relatively low cost – was used to fabricate a set of 4×4 mm microstructured BC-DSC electrodes. The relationships between the laser ablation size precision, the quality of the FTO film, and the UV laser ablation parameters were systematically analyzed using a 4×4 orthogonal design and an assistant experimental design. The key parameters and characteristics of laser ablation were also presented in this paper. The incident photon-to-electron conversion efficiency (IPCE) and the current–voltage characteristic of the BC-DSC were also measured to determine the feasibility of the proposed techniques.

## 2. Experimental equipment, materials, and methods

### 2.1. Experimental equipment and setup

The equipment used in this study includes a 355 nm diode-pumped solid-state nanosecond UV laser with 100 kHz high pulse-repetition frequency, 7.5-W average laser power at 25 kHz pulse repetition frequency, and less than 2% average power and pulse-to-pulse energy fluctuations. A beam expander was used to improve the laser beam quality. A 2D galvanometer scanner system was used to control the laser beam orbit. A vacuum chuck was used to fix the glass substrate. A schematic diagram of the workstation used for the laser microfabrication of the FTO thin film is shown in Fig. 2. The focal plane was fixed on the sample surface, and the optical spot size of the focused laser beam was approximately 10 μm in diameter.

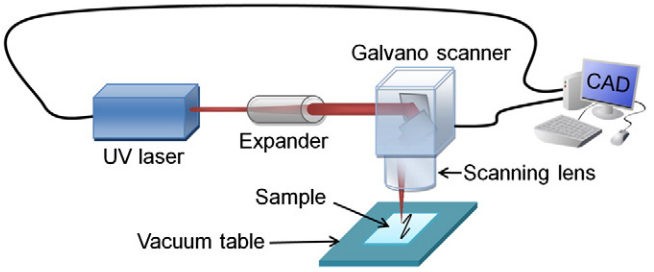

**Fig. 2.** Schematic diagram of the experimental setup for UV laser microfabrication of FTO thin films.

### 2.2. Experimental material and microprocessing graphics

The sheet resistance of the 3.2-mm FTO glass (Nippon Sheet Glass Co. Ltd., Japan) was 10 Ω/cm$^2$, and the thickness of the FTO thin film was 370 nm. The surface morphology of the FTO film is illustrated by a scanning electron microscopy (SEM) image shown in Fig. 3. The FTO film had a grain size of 100–200 nm. The microprocessing graphics required on the FTO thin films were delicate (Fig. 4). A laser ablation curve divided the film into two parts each of that formed an interdigitated finger electrode (one working and one counter electrode). The width and length of each electrode were 15 μm and 4 mm, respectively. The distance between the electrodes was 10 μm. The two electrodes were mutually insulated for greater than 1 MΩ. The electrodes were free of microcracks, and the damage in glass substrate should be as little as possible. Laser microprocessing was the most suitable method to achieve the desired specifications of the microstructured electrodes cost-effectively and efficiently.

### 2.3. Fabrication processes of the BC-DSC

The BC-DSC was fabricated following reported procedures [7]. After the UV laser patterning of the FTO glass substrates, a set of FTO fingers was coated selectively with a platinum layer using a pulsed electrodeposition method. Current pulses (with current on and off durations of 100 and 900 ms respectively) with the current density of 3 mA/cm$^2$ were applied for 200 s. A protective porous layer of ZrO$_2$ nanoparticles was then selectively deposited onto the platinized electrode fingers using an electrophoretic deposition method which has been performed in a colloidal solution containing ZrO$_2$ nanoparticles before [14]. A direct current potential bias of 5 V was applied between the two sets of electrode fingers for 100 s. A mesoporous TiO$_2$ electrode was screen-printed onto the device, followed by a subsequent sintering step [15]. The sintered devices were dyed in N719 dye for 24 h, and were sealed by plain glass cover slides using Surlyn® gaskets. Finally, an electrolyte solution containing triiodide/iodide redox mediator was filled into the device chamber through an entry port on the glass cover slide.

### 2.4. Experimental design

A 4×4 orthogonal experiment was designed to identify and optimize the key parameters in laser ablation (Table 1). The single-scan method was used to ensure the size accuracy and efficiency of the microprocessing. The effects of three factors, namely, the laser output fluence of a single pulse ($E$), the repetition frequency ($F$), and the laser scanning speed ($V$), on the depth and width of the laser-ablated FTO film were evaluated. Each factor was tested at four levels. The width and depth of laser ablation were examined using a mechanical

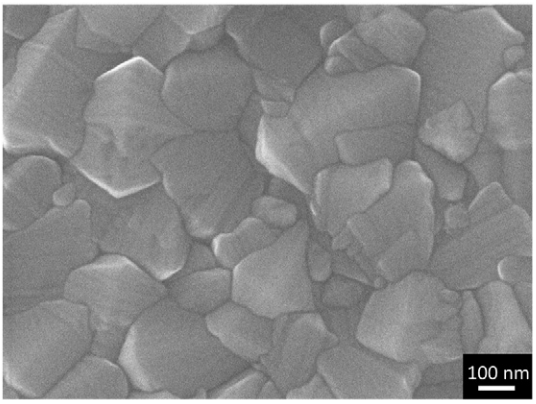

**Fig. 3.** SEM image showing the morphology of the FTO film.