Laser annealed composite titanium dioxide electrodes for dye-sensitized solar cells on glass and plastics

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We report a rapid and low temperature process for fabricating composite TiO2 electrodes for dye-sensitized solar cells on glass and plastics by in tandem spray deposition and laser annealing. A homogenized KrF excimer laser beam (248 nm) was used to layer-by-layer anneal spray deposited TiO2 nanoparticles. The produced TiO2 film is crack free and contains small particles (30 nm) mixed with different fractions of larger particles (100–200 nm) controlled by the applied laser fluence. Laser annealed double-layered structure is demonstrated for both doctor-blade deposited and spray-deposited electrodes and performance enhancement can be observed. The highest demonstrated all-laser-anealed cells utilizing ruthenium dye and liquid electrolyte showed power conversion efficiency of ~3.8% under simulated illumination of 100 mW/cm². © 2009 American Institute of Physics. [DOI: 10.1063/1.3082095]

Dye-sensitized solar cells (DSSCs) are a potential low-cost alternative to conventional solar cells owing to potentially high efficiency (~10%) and low cost fabrication processes. Conventionally, nanoporous TiO2 photoanode is fabricated through blading or screen printing of TiO2 slurry followed by high temperature thermal sintering. TiO2 films are also produced by using spray pyrolysis and polymer pyrolysis. However, these processes involve high temperature. Lowering the processing temperature is required for cell fabrication on flexible substrates. A drawback is that the material produced by simply sintering at lower temperature cannot compete in regard to the electrical properties with standard high-temperature process. Other low temperature processes and corresponding reported efficiencies under illumination of 100 mW/cm² include compression (3%), hydrothermal crystallization (4.2%), chemical vapor deposition with UV treatment (3.8%), microwave irradiation (2.3%), and electron bombardment (2.8%).

Meanwhile, there is also intense interest in engineering composite TiO2 layers to increase open circuit voltage $V_{OC}$ and short circuit current density $J_{SC}$, e.g., layers containing two distinct sizes of particles, nanoparticle/nanorod mixture, and double-layer structure. The reason for increased $J_{SC}$ and $V_{OC}$ is the higher light harvesting and raised Fermi level of the semiconductor due to prolonged residence time of electrons in charge trapping state. In general, it is well accepted that a composite layer is superior to the single layer structure.

In this letter, we report a low temperature method that can produce electrodes with distinct particle size and composite layers via layer-by-layer laser annealing. Laser processing of DSSC has been reported. However, reported cell efficiency is not satisfactory (1.8%) unless a high temperature sintering step is added (4.3%). Recently, we demonstrated the excimer laser annealing (ELA) of metal oxide (ZnO) nanoparticles to improve the electrical properties in producing field effect transistors (FETs). Here, ELA is coordinated with spray deposition to realize DSSC on glass and plastic substrates with performance comparable to high temperature annealed cells.

The TiO2 nanoparticles were deposited and simultaneously annealed by laser on SnO2 coated glass (Hartford Inc.) and ITO coated polyethylene terephthalate (PET) by Delta Technologies as shown in Fig. 1(a). The nanoparticle suspension was prepared by mixing commercially available TiO2 nanopowders (Degussa) in solvent containing water, followed by high temperature polymer pyrolysis. However, these processes involve high temperature annealed cells utilizing ruthenium dye and liquid electrolyte showed power conversion efficiency of ~3.8% under simulated illumination of 100 mW/cm².

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FIG. 1. (Color online) (a) The schematic of in tandem spray deposition and laser annealing setup. (b) The relation between aerosolized nanoparticle suspension volume with deposited film thickness. (c) Optical dark field microscopy image of spray deposited and laser annealed film. (d) Film surface profile measured by a profilometer.

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Nitric acid, Triton, ethanol, and methanol. A collision nebulizer (Ted Pella, Inc.) was used to transfer the suspension into aerosols and the carrier gas, e.g., nitrogen, was regulated by a flow meter (Omega). The aerosol jet impinged on the receiving substrate at an angle of incidence of 45°. A krypton fluoride (KrF) excimer laser (wavelength: 248 nm, pulse width: 20 ns) was used for annealing. A large-area, uniform, top-flat beam profile can be obtained by using a fly’s eye homogenizer to ensure uniform laser annealing. The deposition and annealing were performed inside a sealed chamber. By regulating carrier gas flow rate, an aerosolization rate of ~0.8 mL/min was maintained. The overall thickness of the TiO₂ film monotonically increases with the aerosolized volume as shown in Fig. 1(b). Figure 1(c) shows the obtained porous, macroscopically uniform, and crack-free film. The surface profile [Fig. 1(d)] indicates that the film is nonuniform macroscopically and consists of agglomerates with lateral dimension from a few micrometers up to 100 μm. Nanoparticles carried within the spray droplets tend to form agglomerates if the evaporation of the solvent upon intercepting the substrate is fast compared to the deposition rate.

The annealed film area was 0.35 cm². The films were dipped overnight (~15 h) into a sensitizing 0.3 M dye solution ruthenium 535-bis(tetrabutylammonium) (Solaronix) in ethanol at room temperature. The counter electrodes were made by screen-printing platinum catalyst (Solaronix) on glass/SnO₂ and sintered for 400 °C for obtaining a transparent Pt layer. The Pt electrode and the dye-loaded TiO₂ electrodes were made by screen-printing platinum catalyst and observed to thoroughly wet the dye-covered TiO₂ electrode via capillary action. The current density versus voltage (J-V) characteristics of the cells were measured under AM 1.5 100 mW/cm² illumination from a solar simulator immediately after cell assembly by a semiconductor analyzer (Agilent 4155A).

Figure 2 shows scanning electron microscopy (SEM) micrographs and the x-ray diffraction (XRD) patterns of laser annealed TiO₂ nanoparticles on glass under different laser fluences (with 10 Hz repetition rate). Under the fluence of 33.7 mJ/cm², the particle size in the TiO₂ film remains largely unchanged (~30 nm). The XRD pattern shows that the peak intensity ratio between anatase and rutile decreases slightly (from 3.27 to 2.88) indicating a small fraction of anatase phase is transformed into rutile. Increasing the laser fluence results in the appearance of larger nanoparticles (100–200 nm) due to laser induced melting and coalescence. Correspondingly, the anatase to rutile intensity ratio reduces further to 1.6 with 80.9 mJ/cm² implying further increase in rutile phase. No changes can be found in full width at half maximum of rutile peak upon laser annealing.

Figure 3(a) shows the J-V characteristics for several cells annealed with 80.9 ml/cm² containing varying thickness on glass. In these cells, the short circuit current density (Jsc) rises to ~12 mA/cm² as the TiO₂ thickness is increased to 5.96 μm and reduces upon further thickness increasing. The open circuit voltage (Voc) only decreases slightly (3.8%, the difference is within the label size) when the thickness increases from 2.07 to 5.96 μm and remains approximately the same as thickness increases thereafter. The initial increase in Jsc can be related to the increased surface area of TiO₂ and the amount of adsorbed dye. As the thickness continues increasing, the number of surface recombination centers is also expected to increase and results in reduction in Jsc and Voc.

Figure 3(b) shows the current-voltage (J-V) characteristics for DSSCs on glass with varying laser fluences. The TiO₂ film thickness is ~6 μm. The short-circuit current (Jsc), open-circuit voltage (Voc), fill factor (FF), and power conversion efficiency (PCE) derived from the J-V curves for different cells are also presented in the table in Fig. 3(b). From Fig. 3(b), it can be seen that Jsc is clearly improved over the cells via use of higher laser fluence (from 8.75 to 13.2 mA/cm²). The open circuit voltage remains almost unchanged, resulting in overall efficiency increase from 2.7%
to 3.8%. Laser annealing enhances the neck growth between particles and therefore the electron diffusion coefficient as has been suggested in thermal sintering. At the same time, the presence of larger diffuse particles and the increase in rutile phase resulting from melt-mediated laser annealing enhance scattering as the rutile phase has higher refractive index promoting light harvesting. Both effects contribute to the higher $J_{sc}$ in cells annealed with higher laser fluence shown in Fig. 3(b). However, the larger particles reduce dye loading. Figure 3(c) shows the transmission spectra of the dye-sensitized electrode before cell construction. Examining the transmission at 800 nm shows the scattering is much higher for electrodes processed by higher laser fluence. Considering the scattering offset at 800 nm, the transmission at 500 nm reveals that 80.9 mJ/cm$^2$ incurs the lowest dye loading in agreement with the decrease in surface area. Even with low dye loading, the cell exhibits better efficiency, suggesting higher electrical conductivity and light harvesting resulting from laser annealing. A reference cell fabricated by doctor-blading of $\sim$15 μm TiO$_2$ nanoparticles followed by standard thermal annealing process at 450 °C reveals similar efficiency (4.4%) and fill factor (0.4).

Furthermore, using laser for double-layered structure fabrication is demonstrated. For facilitating the proof of concept, it is first shown for doctor-blade deposited electrode on glass. Two identical TiO$_2$ films were obtained by doctor-blading. One sample was first subjected to two pulses of $\sim$90 mJ/cm$^2$ laser irradiation and then both were annealed at 450 °C for 30 min. The thickness of both films are $\sim$6–7 μm as measured by a surface profilometer. Laser annealing gives rise to a diffusive and dense top layer ($\sim$1 μm thick) consisting of larger TiO$_2$ clusters of a few hundred nanometers, as indicated in the SEM micrograph in Fig. 4(a). Multiple cells with an active area of $\sim$3.3 cm$^2$ were fabricated and $J$-$V$ curves show an average $\sim$24% enhancement of short-circuit current $J_{sc}$ for laser annealed double-layered films [Fig. 4(b)]. This can be attributed to the increase in optical thickness and enhanced electrical property of the films by laser annealing. Second, cells were fabricated on ITO/FET by in tandem spray and laser annealing. Due to the lower damage threshold on plastics, a laser fluence of 60.7 mJ/cm$^2$ was used. Considering the laser radiation penetration depth in TiO$_2$ films, predeposited layer $>$3 μm should be enough to prevent substrate damage from laser annealing. Based on this concept, a double-layered structure was also fabricated, whereby laser fluence was increased to 80.9 mJ/cm$^2$ after formation of a $\sim$3 μm layer as illustrated by the inset in Fig. 4(c). With this structure, a slight increase in efficiency from 3.2% to 3.3% was observed. The fact that laser annealing enhances light trapping and electron transport and therefore augments $J_{sc}$ as shown by both doctor-blade deposited and spray-deposited double-layered structures, suggests further optimization is possible.

In conclusion, a low temperature method for producing crack free composite electrodes by laser annealing is proposed. This technique not only realizes DSSCs on temperature sensitive substrates, but also enables full three-dimensional engineering of nanoporous structure. By employing sources offering larger processing area such as high power industrial lasers or excimer lamp and translation systems, this technique can be adapted to roll-to-roll manufacturing.

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**FIG. 4.** (Color online) (a) The cross-sectional and top view (inset) of double-layered structure. (b) The $J$-$V$ curves of the cells with and without laser annealing under illumination of 24 mW/cm$^2$. The inset shows the comparison of averaged short circuit current. (c) The $J$-$V$ curves of cells fabricated on plastic substrate.