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Laser plasma sintering for fabricating indium tin oxide thin films

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ABSTRACT

This paper introduces laser plasma sintering (LPS), and uses it to fabricate dense indium tin oxide (ITO) thin films. LPS uses a nanosecond pulsed laser to generate an airborne laser-induced plasma (LIP) of high temperature and high pressure, which sinters the particles on the substrate. ITO thin films were fabricated by spin-coating ITO nanoparticle (NP) ink onto a substrate then using the LIP to sinter the NPs. The deposited NPs are sintered by the combined effect of the thermal radiation from the LIP and the impact of the shockwave. This LPS process could generate a polycrystalline structure with an average grain size of 280 nm. The electrical resistivity of the film was decreased to ~1/1000 of the initial value without losing transparency of the ITO film. The minimum resistivity of 1.6×10^{-5} Ω·m was obtained significantly reducing the optical transparency of the ITO film. The thickness of the sintered layer and electrical resistivity could be controlled by adjusting the process parameters. LPS also strengthened the adhesion between the sintered film and the substrate significantly, compared with the conventional thermal or laser sintering process. This work suggests that LPS process can be an effective tool to fabricate various thin films with enhanced crystallinity and adhesion characteristics.

1. Introduction

Transparent conductive oxides (TCOs) are used many devices, including displays, solar cell panels, flexible electronics, and photovoltaics. Therefore, development of effective methods to fabricate thin TCO films of high quality has been an important goal [1–4]. Indium tin oxide (ITO) is a widely used TCO, due to its high conductivity and transmittance [5–7], and several techniques have been developed to synthesize ITO films. Sputtering is widely used, but it has several demerits, including complex equipment, difficulty in vacuum conditioning, material waste, and difficulty of post treatment [8–10]. Ink-jet printing does not suffer from these demerits [11,12]. The method uses ITO nanoparticle (NP) ink, i.e., well-suspended colloidal ITO NPs. Because the process enables direct patterning of ITO thin films, and it is relatively inexpensive. Also, the process does not involve high temperature, so it can be easily used for flexible organic substrates. However, in many practical applications, the deposited film has insufficient electrical conductivity, so additional post-treatment is required [13,14], which is generally a thermal treatment termed annealing [15,16]. Thermal annealing is widely used in ITO thin-film fabrication [17,18], but the process entails high temperature and long process time, so it is not applicable when substrates can be damaged by heat.

Laser sintering has advantages such as reduced thermal effects and capability of selective treatment, and therefore may be a viable alternative to thermal sintering [19,20]. For ITO thin films, various laser sintering processes combined with wet coating have been proposed. CO_2 laser sintering combined with a doctor blade method was used to form 3-μm-thick ITO films on flexible substrate with a sheet resistance $R_s = 400$ Ω/□ [21]. A pulsed (0.2–20 ms) Nd:YAG laser sintering process combined with a spin-coating technique produced 800-nm-thick ITO films with $R_s = 640$ Ω/□ [16]. A similar process that uses a KrF excimer laser could fabricate thin films of variable thickness up to 200 nm with $R_s = 540$ Ω/□ [22]. Possibly because of the reduced thermal effects due to the brevity of heating, laser-sintered samples have lower R_s than do samples produced by sputtering. Laser sintering, may generate voids and cracks in the layer, and they degrade its mechanical and electrical properties [23]. The adhesion of the sintered thin film has been little investigated even though it is a critical factor in practical applications [24].

Here we propose a sintering process entitled laser plasma sintering (LPS). Although various laser sintering processes based on direct laser heating of particles, no laser sintering process used a combined effect of thermal heating and mechanical impact simultaneously. We employed laser-induced breakdown (LIB) plasma which has both thermal and mechanical effects at the same time. When a high-intensity laser pulse is focused in air, LIB of air occurs, generating laser-induced plasma (LIP). The core temperature of plasma increases up to ~10^5 K at the end of the laser pulse [25]. Expansion of the high-temperature

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plasma generates a shockwave which impinges onto a sample. We utilized the thermal effect as well as the mechanical impact of the shockwave to induce sintering. The temperature of shockwave front was calculated to be in the range from 1000 to 10,000 K. When the distance between the plasma core and the substrate was controlled appropriately, the shockwave impact and the thermal effect could sinter particles more effectively than the typical thermal sintering process. LPS sintering process was employed to fabricate ITO films of enhanced crystalline and adhesion properties, more specifically to achieve $R_s < 100\ \Omega/\square$ and to substantially increase adhesion strength without losing transparency.

2. Experiment

2.1. Sample preparation

Commercially-available ITO NPs (Sigma Aldrich, nominal diameter < 50 nm, nominal purity 99.9%) were used to prepare NP ink. The measured mean diameter of the NPs was 22 nm, and The melting point was $941 \le T \le 1311$ °C as determined using differential scanning calorimetry [22], which is substantially lower than the melting temperature of bulk ITO (1910 °C). ITO NPs were mixed with ethanol to prepare ITO suspension (10% ITO *w*/*w*). The solution was homogenized by sonication in an ultrasonic bath for 30 min, then stirred using a magnetic stirrer for 24 h. ITO NPs were deposited by spin coating on Si and PET substrates (1200 rpm, 30 s). The ITO film thickness was adjusted to be 200 nm by controlling the volume of the liquid droplet. The film was dried in ambient air for 30 min.

2.2. Laser plasma sintering (LIPS) process

A Q-switched Nd:YAG laser beam (wavelength $\lambda = 1064$ nm, full width at half maximum (FWHM) = 6 ns) was delivered parallel to the substrate and was focused in the air above the sample using a convex lens of focal length $f = 10$ cm (Fig. 1). The laser trajectory before focusing was set to be parallel to the substrate. We used a short-focal length lens to induce strong LIP and therefore the laser beam after the focal plane diverges and eventually hits the surface if the sample size is large. Accordingly, the *h* values were controlled to prevent the collision of the beam with the substrate. We set the half width of the sample to 2 cm to avoid the collision. We processed half of the sample first and then processed the other half after rotating the sample. Small portion of laser energy is not absorbed in the plasma and passes through it. This small energy might hit the substrate after they travel long distance but its amount is less than 10% and this energy is too small to induce additional change on the substrate [26].

The laser pulse energy *E* before passing through the lens was controlled to be 100, 150, or 200 mJ. Hence the intensity of the focused laser beam $I = 2.25 \times 10^{13}$ W/cm^2 is large enough to induce a high-temperature (7000 K when it collides with the surface), high-pressure (~10 MPa) plasma, the expansion of which generates a shockwave [25]. While the thermal radiation from the LIB melts the ITO NPs over a time scale of ~10 μs [27], the shockwave generated by expansion of the LIB strikes the NPs on the sample (Fig. 1). In general, the combined effect of heat and pressure reduces the size and the number voids in the sintered film [28]. It has been reported that increased pressure enhances the sintering performance [29]. When sintering NPs, $P > 1$ MPa can improve the mechanical properties of sintered samples [30]. In this work the shockwave had $P > 1$ MPa and contributed to the densification of particles.

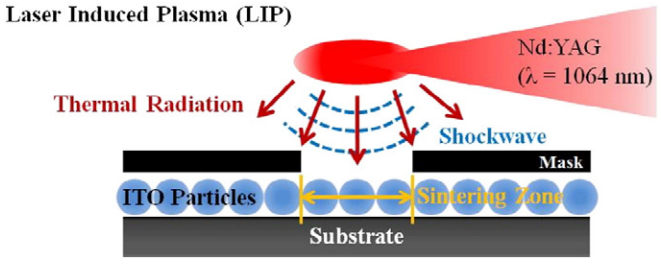

Fig. 1. Schematic diagram of laser induced plasma sintering with ITO nano-particle coated substrate.

To estimate the shockwave intensity in LPS, the shockwave propagation was captured by laser flash shadowgraphy using a N_2 pumped dye laser ($\lambda = 440$ nm, $\tau =$ ns, Fig. 2). The measured vertical length of the laser-induced breakdown plasma was 800 μm. The gap distance *h* between the focal point of the laser beam and the surface was varied in the range of 400–800 μm. The shadowgraphs were captured every 20 ns to measure the velocity of the shockwave. Then *P*, density ρ, and temperature *T* of the shockwave were calculated using blast wave theory [31]:

$$P = P_0 + (1-\rho_0/\rho)\rho_0(U-c)^2, \tag{1}$$

$$\rho/\rho_0 = (\gamma+1)/\left(\gamma-1+2M^{-2}\right), \tag{2}$$

$$\frac{T}{T_0} = \frac{P}{P_0}\left[\left(\frac{\gamma+1}{\gamma-1}\right)+P/P_0\right]\Big/\left[1+\left(\frac{\gamma+1}{\gamma-1}\right)\times P/P_0\right], \tag{3}$$

where P_0, ρ_0, and T_0 are pressure [Pa], density [kg·m^{-3}] and temperature [K] of the ambient air, respectively, *U* is the shockwave speed [m·s^{-1}], *c* is the speed of sound [m·s^{-1}], γ adiabatic coefficient of air [dimensionless], and *M* Mach number [dimensionless]. Under typical conditions of LPS the estimated temperature and pressure of the shockwave front were 1000–7000 K and 1–16 MPa (Fig. 3).

The width of the sintering zone was set 800 by 800 μm by using a mask. When the laser energy is focused on a small spot and plasma is generated, the air around it expands in all direction. When this shockwave front hit the substrate vertically it pressed the nanoparticles and enhance the adhesion between the nanoparticles and substrate. When the direction of shockwave propagation and the substrate had incident angle, however, the nanoparticles on the substrate were blown away by the drag force. We needed to restrict the process area to prevent the loss of nanoparticle. The particles which were not located right below of the plasma were blown away when we did not apply the mask below the plasma. To fabricate a film of large area, the surface was scanned using a motorized stage system. The number *N* of laser pulses applied to a single spot (superposition number) was varied in the range of 1–30

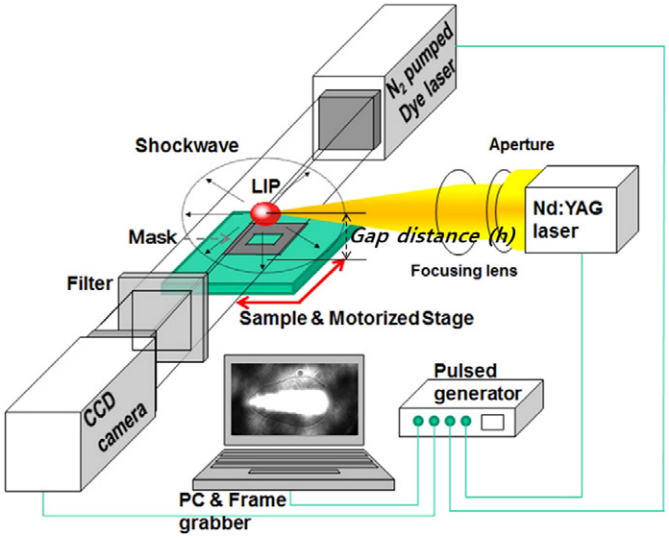

Fig. 2. Experimental set-up of the laser plasma sintering.