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# Formation of indium tin oxide film by wet process using laser sintering

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## ABSTRACT

Indium tin oxide (ITO) films were prepared via a very simple and low-cost preparation technique based on a wet process using a continuous wave (CW) laser and an indium tin (In–Sn) alloy nanoparticle ink. The formation of continuous transparent conductive films using a laser sintering method and micropatterning of the ITO films using a laser direct writing method were investigated. This process is simpler than the conventional two-step heat treatment method and other wet processes that use ITO nanoparticles as starting materials. In addition, the optical and electrical properties of the ITO films were improved. Notably, the conductivity and transmittance were remarkably influenced by the processing parameters, including the laser power and scan speed. Suitable processing conditions were thus investigated and optimized, and ITO micropatterns with accurate linear and sharp edge profiles were obtained by controlling the laser power and focusing conditions in the laser direct writing process.

## 1. Introduction

Indium tin oxide (ITO) thin films are wide band gap semiconductors with good electrical and optical properties such as low resistivities ($\sim 10^{-4}\ \Omega\,\mathrm{cm}$), high carrier concentrations, high mobility rates, and high transparency in the visible and near-infrared regions (450–1100 nm), as discussed by Qi et al. (2009) and Chen et al. (2013). Because of their optical and electrical performance, ITO films have found use in many applications such as in solar cells, inorganic and organic light emitting devices, liquid crystal displays, and laser diodes, as described by Cao et al. (2013). So far, many techniques have been developed to prepare ITO thin films of which vacuum-assisted processes are the most widely used. For example, electron-beam evaporation and DC and RF sputtering methods have been studied by Ali et al. (2005), Ahn et al. (2014), and Kavei and Gheidari (2008), respectively. However, owing to the increasing cost of indium metal, the inefficiencies in terms of material utilization of traditional thin-film deposition procedures, and their high fabrication costs, much effort has been devoted to synthesizing ITO films via solution-based processes. Mahmood et al. (2013) prepared a bilayer film composed of an upper-layer of aluminum-doped ZnO (AZO) and a lower-layer of ITO using an atmospheric pressure-based electrospraying method. A method for the preparation of mesoporous ITO thin films via dip-coating was also proposed by Graberg et al. (2011).

In addition, techniques based on the use of solutions containing dispersed crystalline ITO nanoparticles, which had not been widely used previously, have been developed. Goebbert et al. (1999) reported ITO films with a resistivity of $1.5 \times 10^{-2}\ \Omega\,\mathrm{cm}$ obtained via the sintering of crystalline nanoparticles at temperatures as high as 900 °C. Ederth et al. (2002) reported the electrical and optical properties of thin films prepared by spin coating a dispersion of nanosized ITO particles. An ITO film with a resistivity of approximately $1 \times 10^{-1}\ \Omega\,\mathrm{cm}$ and a transmittance exceeding 90% was obtained after annealing in a vacuum at 200–400 °C for 2 h and subsequently in air at 500 °C for 2 h. Porous thin films comprised of ITO nanoparticles were prepared by Ederth et al. (2003) using a spin-coating method followed by annealing and reported to have electrical resistivities in the order of $10^{-2}\ \Omega\,\mathrm{cm}$. Inkjet-printing, in which an ink or paste composed of ITO nanoparticles, solvent, and additives is used to prepare ITO films, is another wet process using ITO nanoparticles that has been extensively researched in the last few years as an approach for simplifying the process and reducing the cost of ITO film fabrication. Hwang et al. (2011) reported that an inkjet-printed film with a thickness of 580 nm prepared using an ITO nanoparticle ink exhibited a sheet resistance of 517 Ω/sq after annealing at 400 °C. Kölpin et al. (2013) presented a conceptual design for ITO inkjet inks for the manufacture of electronic devices

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with ITO nanoparticles effectively stabilized in different dispersion media.

One of the problems with using ITO nanoparticles is the rather high sintering temperature required to form conductive transparent films, which limits the choice of substrate. It is necessary to lower the sintering temperature if polymer substrates with low thermal resistances are to be used. Ohsawa et al. (2011) developed a low-temperature process using a nanoparticle ink containing indium tin (In–Sn) alloy nanoparticles instead of ITO particles as the starting material (see also their patent, Ohsawa and Hayashi, 2011). The several nanometer-diameter In–Sn alloy nanoparticles were prepared using a gas evaporation method as described by Hong and Han (2006). The developed ink consisted of In–Sn alloy nanoparticles dispersed stably in a mixture of organic solvents and enabled the formation of a conductive transparent film via sintering at temperatures ranging from 200 to 300 °C. The two-step procedure involved vacuum heating at 230 °C and 8 Pa for 60 min followed by heating in air at 230 °C for 30 min. In the first step, the In–Sn nanoparticle film was converted into a continuous In–Sn alloy film, which was conductive but had low transparency. A transparent conductive ITO film was then formed via the oxidation of the continuous In–Sn alloy film in the second step. The resistivity of the film was $1.1 \times 10^{-2}\ \Omega\,\mathrm{cm}$, and its transmittance at 550 nm was 95%. It should be noted that ITO films prepared via the sintering of ITO nanoparticles have porous structures consisting of more-or-less-sintered nanoparticles, rather than continuous and homogenous structures (Ederth et al., 2002). On the other hand, the ITO film prepared from the In–Sn alloy nanoparticles did exhibit a continuous and homogenous structure because of the lower sintering temperature compared with that required for oxide nanoparticles.

However, compared with a simple inkjet printing process, the two-step, low-temperature process using an ink consisting of In–Sn alloy nanoparticles requires control of a gas atmosphere and an extended time for thermal annealing, which are not desirable with respect to the minimization of the environmental impact, process costs, and energy consumption. Previously, we reported the laser processing of metal nanoparticle inks and the formation of highly conductive metallic micropatterns and films. Laser processing has emerged as an attractive technique for microelectronics fabrication because of its advantageous features, including high resolution, high speed, minimal environmental impact, and a high degree of flexibility to control the resolution and size of the micropatterns. Watanabe et al. (2005) and Aminuzzaman et al. (2008) reported that the linewidth of an silver (Ag) microwire could be controlled flexibly by changing the objective lens characteristics when an Ag nanoparticle ink was used as the starting material for laser sintering, enabling the production of submicron Ag wiring through an objective lens with a high numerical aperture (N.A.) value. Conductive Ag micropatterns and metal nanoparticle/polyhedral-oligomeric-silsesquioxane (POSS) hybrid films have also been fabricated via laser processing, as described in Aminuzzaman et al. (2010) and Watanabe et al. (2012), respectively. Previously (Watanabe et al., (2009)), we showed that laser energy in the visible region was efficiently absorbed by the plasmon band of metal nanoparticles. Specifically, the confined energy in thermally isolated metal nanoparticles several nanometers in diameter caused a rapid temperature rise and efficient conversion of the metal nanoparticles into a conductive metal film. Watanabe and Qin (2014) also reported that laser sintering was effective for the formation of a homogeneous and highly conductive film from metal nanoparticles because of reduced grain growth during the high-speed process. In this paper, a simple wet process (spin coating) using an In–Sn alloy nanoparticle ink was performed followed by laser sintering with a 1064 nm wavelength continuous wave (CW) laser to form the continuous conductive transparent ITO film with a homogeneous morphology. Notably, a metal oxide film was prepared instead of a pure metal film. During the fast sintering process, fusion and oxidation of the nanoparticles was achieved, leading to the formation of a transparent conductive ITO film via a one-step sintering process. In addition, the laser sintering process could be performed in air, while careful control of the atmosphere was necessary in the traditional sintering process. The influence of the laser sintering conditions on the microstructure, resistivity, and optical properties of the ITO film were also studied.

Owing to its high optical transmittance and conductivity, patterned ITO has been applied as an electrode material in order to enhance the current spreading uniformity, as reported by Lin and Hsu (2014). However, conventional patterning technologies (e.g., wet-etch lithography, selective deposition, chemical vapor, and photolithography) are costly because they require multiple steps. Among them, laser ablation is widely applied for the patterning of ITO films because it allows for non-contact processing, high speeds, and dry processing. Bian et al. (2013) selectively removed 120–160 nm thick ITO thin films from glass substrates using a femtosecond laser. Kuang et al. (2012) reported the high-throughput surface direct microstructuring of ITO on glass via parallel processing using diffractive multiple ultrashort pulse laser beams with $\lambda = 1064$ nm and $\tau_p = 10$ ps. In practice, ITO is fabricated as a continuous thin film coating followed by local removal using patterning technologies as mentioned above to create functional structures for specific applications. In this paper, an ITO pattern was readily fabricated using a laser direct writing process and a CW laser. Laser direct writing based on CW laser irradiation of an In–Sn alloy nanoparticle film was simpler than laser ablation because formation and micropatterning of the transparent conductive ITO film were achieved simultaneously.

## 2. Experimental

The In–Sn alloy nanoparticle ink was purchased from ULVAC, Inc. (ITO nanometal ink, ITO1Cden, solvent: tetradecane, In–Sn alloy nanoparticle content in the ink: 20.4 wt%, Sn content in the In–Sn alloy: ~10 wt%, ULVAC Inc., 2014). The In–Sn alloy nanoparticle ink was produced using a gas evaporation method (gas phase condensation) with an average particle size of approximately 4 nm, and the nanoparticles were individually dispersed in tetradecane. The nanoparticle surface was modified with a fatty acid methyl ester derivative to prevent agglomeration during preparation, as reported by Ohsawa et al. (2011) and Ohsawa and Hayashi (2011). Prior to coating, the glass substrate was subjected to ultrasonic cleaning with acetone and methanol and then irradiated using deep UV (Photo surface processor, PL16-110, Sen Light Corp.) for 10 min to introduce hydroxyl groups on the surface and therefore increase its hydrophilicity and improve the binding force between the substrate and the nanoparticles. Spin coating was performed in a spin coater (MS-A100, Mikasa Co., Ltd) at a rate of 2000 rpm for 30 s at RT in air, and the obtained film was dried at 110 °C for 30 s on a hot plate before laser irradiation.

The laser source employed in this study was a CW DPSS laser (1064 nm 5 W, CNI). For continuous transparent conductive film formation, laser sintering was performed by scanning with a line-shaped laser beam that was shaped using a beam expander and a cylindrical lens. The line-shaped beam was focused on the precursor In–Sn alloy nanoparticle film through an achromatic lens (NYTL-30-30PY1, SIGMA KOKI). The focused laser beam was irradiated on the precursor film by raster scanning using an automated xyz-translation stage controlled by a computer. The experimental setup is schematically illustrated in Fig. 1. During laser-beam scanning, the sintering process was observed using a charge-coupled device (CCD) camera.